Synthesis and Emission Behavior of 1,3-diarylisobenzofuran-5,6-dicarboximides and Their Transformation into Naphthalene-2,3:6,7-bis(dicarboximide)s

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Abstract: Phosphine-assisted annulation of 2,5-diarylfuran-3,4-dicarbaldehydes with maleimides provided the title isobenzofurans in satisfactory yields. An effect of the substituents at the para position of the aryl groups in these isobenzofurans was demonstrated clearly by a red shift in their UV-vis absorption and emission spectra. They were transformed into the corresponding naphthalene-2,3:6,7-bis(dicarboximide)s by Diels-Alder reaction with another maleimide and subsequent dehydration with the aid of trifluoromethanesulfonic acid. Emission behavior of the title bis(dicarboximide)s is also described.

Keywords: Isobenzofuran, Naphthalene-bis(dicarboximide)s, Furan-3,4-dicarbaldehydes, Substituent Effect, Dehydration, Diels-Alder Reaction

1. Introduction

Arene-dicarboximides show interesting photochemical and photophysical properties, such as photoreduction [1, 2] photocycloaddition [3, 4], and photo-excited emission [5–8]. Heagy *et al*. reported that dual fluorescent naphthalene-2,3-dicaboximides could be used in white organic light-emitting devices (OLEDs) [9]. Also, we reported synthesis of various 1,6-methano [10] annulene-3,4-dicaboximides and their emission behavior [10]. The results indicate that arene-dicarboximides are promising agents for electronic materials. Arene-dicarboximides can be obtained by several simple ways, such as condensation of anhydride with amine [11, 13–15] and Gabriel reaction of *N*-unsubstituted dicarboximide with alkyl or aryl haide [16-18]. Besides, an approach by Diels-Alder reaction via arene-*o*-quinodimethane or isobenzofuran constructing concomitantly another benzene ring has been reliable [19–22]. In 1979, Haddadin *et al*. reported an interesting synthetic method, in which

o-phthaldehyde (1) reacts with *N*-phenylmaleimide (3) in the presence of triethylphosphite to give *N*-phenylnaphthalene-2,3-dicarboximide (2) in a satisfactory yield (62%) [23]. However, application to synthesis of anthracene- 2,3-dicarboximide from 2,3-naphthaldehyde (4) by this method resulted in a low yield (35%) of the product 5. Notwithstanding the fascinating methodology based on the result of the Haddadin *et al*., there had been no work of its improvement reported for a long time. We reported the improved method for the Haddadin's annulation, that is, we found that various naphthalene- and anthracene-dicarbox-imides were obtained in good yields under the conditions with trioctylphosphine, instead of triethylphosphite, in re- fluxing dioxane (Scheme 1) [24]. We have applied our improved method to synthesize the title heterocyclic com pounds. In this paper, we describe the synthesis of the 1,3-diarylisobenzofuran-5,6-dicarboximides (6–8) and their

transformation to naphthalene-bis(dicarboximide)s.
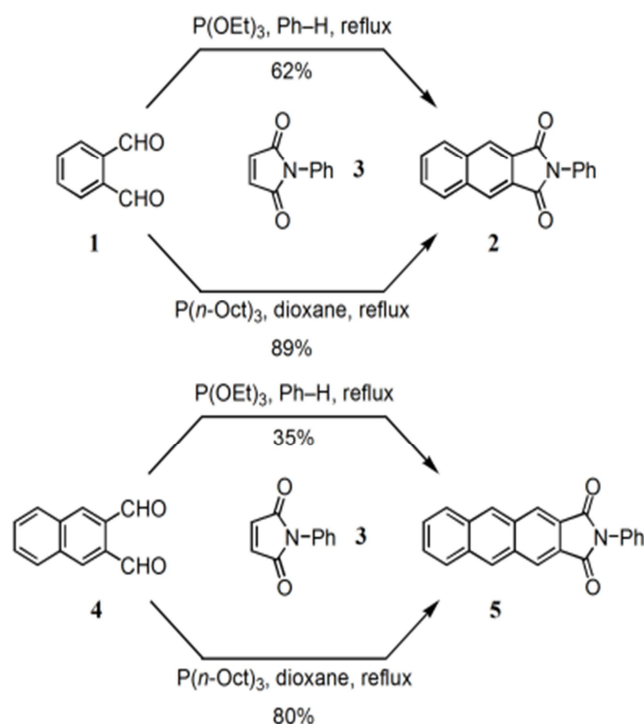
Scheme 1. *Synthetic methods for arene-dicarboximides 2 and 5.*

2. Experimental

2.1. 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. Emis-sion quantum yields were obtained by comparison with that of anthracene ($\Phi = 27\%$ in ethanol). ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL λ400 and ECA500 spectrometers. Chemical shift values of tetramethylsilane ($\delta = 0$ ppm) for ^{1}H-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, tetrahydrofuran (THF) and triethylamine were purchased from Kanto Chem. and were distilled over CaH$_2$. Dichloromethane (DCM), chloroform, dichloroethane (DCE), and acetonitrile were also purchased from Kanto Chem. and were distilled over P$_2$O$_5$. Trioctylphosphine, *N*-methylmaleimide, *N*-ethylmaleimide, *N*-cyclohexylmaleimide, *N*-phenylmaleimide, and trifluoromethanesuifonic acid were purchased from Tokyo Chemical Industry, Inc. Oxalylchloride, LiAlH$_4$, and thionylchloride were purchased from Wako Chem. *N-p*-Anisylmaleimide was prepared according to a two-step procedure from maleic anhydride and *p*-anisidine reported by Cava *et al.* [30–31] 2,5-Diarylfuran-3,4-dicarbaldehydes were prepared according to a procedure reported by Wang *et al.* [25]

2.2. General Procedure for Synthesis of 2,5-diarylfuran-3,4-dicarbaldehydes

A solution of 2,5-diaryl-3,4-bis(methoxycarbonyl)furan (19.0 mmol) in 70 mL of THF was added slowly to a suspension of 1.14 g of LiAlH$_4$ (30.0 mmol) in 50 mL of THF at 0ºC. After being stirred at room temperature for 30 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 Na$_2$SO$_4$ and the solvent was evaporated to give the crude corresponding diol, which was used without further purification in the next Swern oxidation.

A solution of dimethylsulfoxide (2.8 mL) in 7 mL of DCM was added dropwise to a solution of oxalylchloride (1.50 mL, 17.7 mmol) in 40 mL of DCM at –80ºC, followed by addition of a solution of the diol (5.90 mmol) in 5 mL of DMSO and 15 mL of DCM, and then triethylamine (11 mL). After being stirred at the same temperature for 3 h, the resulted reaction mixture was poured into water (100 mL) and was extracted with DCM (30 mL x 3). The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. The solvent was removed and the residual solids were purified by recrystallization from hexane/DCM to give the dialdehyde.

9 (75% from 12): Colorless needles, m.p. 137–138ºC (lit. [32] 126–128ºC). ^{1}HNMR (500 MHz, CDCl$_3$) $\delta = 10.44$ (s, 2H), 7.98 (m, 4H), 754 (m, 6H) ppm; ^{13}CNMR (CDCl$_3$, 125 MHz) $\delta = 186.8, 159.4, 131.0, 128.9, 128.6, 127.9, 121.4$ ppm; IR (KBr) $\nu = 1686$ (vs), 1671 (vs) cm^{-1}.

10 (77% from 13): Yellowish powder, m.p. 137.5–138.5ºC. ^{1}HNMR (CDCl$_3$, 500 MHz) $\delta = 10.4$ (s, 2H), 7.86 (d, $J = 8.3$ Hz, 4H), 7.33 (d, $J = 8.3$ Hz, 4H), 2.45 (s, 6H) ppm; ^{13}CNMR (CDCl$_3$, 126 MHz) $\delta = 186.9, 159.6, 141.5, 129.6, 128.5, 125.2, 120.9, 21.6$ ppm; IR (KBr) $\nu = 1685$ (vs), 1677 (s), cm^{-1}; MS m/z (%) = 304 (M$^+$, 100), 276 (46), 261 (13), 119 (42), 91 (23), 65 (6). HRMS calcd for C$_{20}$H$_{16}$O$_3$ (M$^+$) 304.1099, found 304.1106.

11 (79% from 14): Yellow powder, m.p. 147–148ºC. ^{1}HNMR (500 MHz, CDCl$_3$) $\delta = 10.41$ (s, 2H), 7.95 (dt, $J = 9.0$, 2.5 Hz, 4H), 7.04 (dt, $J = 9.0$, 2.5 Hz, 4H), 3.90 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) $\delta = 186.9, 161.7, 159.4, 130.2, 120.5, 120.2, 114.3, 55.5$ ppm; IR (KBr) $\nu = 1682$ (s), 1668 (vs) cm^{-1}; MS m/z (%) = 336 (M$^+$, 100), 308 (24), 293 (29), 167 (7), 149 (18), 135 (40), 77 (6). HRMS calcd for C$_{20}$H$_{16}$O$_5$ (M$^+$) 336.0998, found 336.1002.

2.3. 1,3-diarylisobenzofuran-5,6-dicarbaldoxime 6–8

To a solution of the 2,5-diaryl-furan-3,4-dicarbaldehyde (0.5 mmol) and *N*-substituted maleimide (0.55 mmol) in 2 ml of dry dioxane was added trioctylphosphine (0.60 mmol). The mixture was refluxed on a preheated oil bath under nitrogen atmosphere for 0.5–2 h, and was cooled to ice-bath temperature. The crystals formed were collected by suction filtration and washed well with cold ether to give the product. If necessary, the filtrate was concentrated under vacuum and the residue was purified by silica gel chromatography with a solvent system of chloroform/ethyl acetate (or

chloroform/ethanol). The yields are shown in Table 1.

6a: Orange needles, m.p. 285–288ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.51 (s, 2H), 8.00 (d, J = 8.6 Hz, 4H), 7.56 (m, 6H), 7.50 (dm, J = 7.4 Hz, 2H), 7.44 (tm, J = 7.4 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 159.3, 141.9, 124.9, 122.9, 122.3, 122.1, 121.9, 121.3, 119.6, 119.4, 118.7, 114.6, 113.0 ppm; IR (KBr) ν = 1771 (m), 1703 (vs) cm^{-1}; UV-vis (CH$_3$CN) λ_{max} = 240sh (log ε = 4.23), 262sh (4.22), 293 (4.29), 314sh (4.17), 331sh (3.91), 356sh (3.39), 369sh (3.58), 388sh (3.79) 419 (3.91), 441sh (3.89) nm; MS m/z (%) = 415 (M$^+$, 100), 268 (17), 138 (13). HRMS calcd for C$_{28}$H$_{17}$NO$_3$ (M$^+$) 415.1208, found 415.1212.

6b: Orange solids, m.p. 275–278ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.40 (s, 2H), 7.97 (dd, J = 7.9, 1.2 Hz, 4H), 7.55 (tm, J = 7.9 Hz, 4H), 7.43 (tt, J = 7.9, 1.2 Hz, 2H), 3.24 (s, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.3, 148.6, 129.9, 129.2, 128.7, 126.8, 125.5, 121.3, 118.9, 24.3 ppm; IR (KBr) ν = 1761 (s), 1712 (vs) cm^{-1}; UV-vis(CHCl$_3$) λ_{max} = 245 (log ε = 4.20), 251sh (4.20), 271sh (4.24), 283 (4.32), 310sh (4.06), 329sh (3.90), 420 (3.99), 442sh (3.99) nm; UV-vis (CH$_3$CN) λ_{max} = 223 (log ε = 4.32), 241sh (4.22), 251sh (4.22), 263sh (4.25), 280 (4.37), 315sh (4.05), 329sh (3.91), 415 (4.01) 436 (4.01) nm; MS m/z (%) = 353 (M$^+$, 100), 268 (6), 239 (22), 177 (6), 134 (8), 77 (6). HRMS calcd for C$_{23}$H$_{15}$NO$_3$ (M$^+$) 353.1052, found 353.1057.

6c: Orange solids, m.p. 253–255ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.37 (s, 2H), 7.96 (dm, J = 7.9 Hz, 4H), 7.54 (tm, J = 7.9 Hz, 4H), 7.42 (tt, J = 7.9, 1.4 Hz, 2H), 3.80 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.1, 148.6, 130.0, 129.2, 128.7, 126.9, 125.6, 121.4, 118.9, 33.2, 13.8 ppm; IR (KBr) ν = 1750 (s), 1712 (vs) cm^{-1}; MS m/z (%) = 367 (M$^+$, 100), 268 (6), 239 (17), 176 (7), 134 (11), 77 (6). HRMS calcd for C$_{24}$H$_{17}$NO$_3$ (M$^+$) 367.1208, found 367.1205.

6d: Orange solid, m.p. 278–281ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.49 (s, 2H), 8.00 (dm, J = 7.5 Hz, 4H), 7.56 (tm, J = 7.5 Hz, 4H), 7.43 (tt, J = 7.5, 1.4 Hz, 2H), 7.40 (dm, J = 9.2 Hz, 2H), 7.05 (dm, J = 9.2 Hz, 2H), 3.87 (s, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.5, 159.3, 148.8, 130.0, 129.3, 128.8, 127.9, 126.5, 125.7, 124.5, 121.6, 119.8, 114.5, 55.5 ppm; IR (KBr) ν = 1766 (s), 1706 (vs) cm^{-1}; MS m/z (%) = 445 (M$^+$, 100), 268 (15), 239 (10), 223 (8). HRMS calcd for C$_{29}$H$_{19}$NO$_3$ (M$^+$) 445.1314, found 445.1313.

7a: Reddish orange powder, m.p. 294–296ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.47 (s, 2H), 7.88 (d, J = 8.1 Hz, 4H), 7.54 (tm, J = 7.6 Hz, 2H), 7.49 (dm, J = 7.6 Hz, 2H), 7.43 (tt, J = 7.6, 1.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 4H), 2.45 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.3, 148.8, 139.0, 132.0, 130.0, 129.1, 128.2, 127.3, 126.6, 126.0, 125.6, 121.1, 120.1, 21.5 ppm; IR (KBr) ν = 1762 (m), 1711 (vs) cm^{-1}; UV-vis (CH$_3$CN) λ_{max} = 242sh (log ε = 4.34), 265sh (4.29), 281 (4.31), 301 (4.36), 320sh (4.24), 339 (3.90), 356 (3.39), 369sh (3.57), 388sh (3.81), 427 (3.98), 460sh (3.95) nm; MS m/z (%) = 443 (M$^+$, 100), 296 (11). HRMS calcd for C$_{30}$H$_{21}$NO$_3$ (M$^+$) 443.1521, found 443.1519.

7b: Reddish orange solids, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.32 (s, 2H), 7.83 (d, J = 7.9 Hz, 4H), 7.33 (d, J = 7.9 Hz, 4H), 3.21 (s, 3H), 2.44 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.4, 148.6, 138.9, 129.9, 127.3, 126.4, 125.5, 120.9, 119.2, 24.3, 21.5 ppm; IR (KBr) ν = 1755 (vs), 1716 (vs), 1701 (vs) cm^{-1}; UV-vis (CH$_3$CN) λ_{max} = 223 (log ε = 4.50), 240sh (4.31), 267sh (4.26), 281 (4.32), 292sh (4.28), 319sh (4.08), 338sh (3.82), 369sh (3.62), 388 (3.82), 420 (3.96), 447sh (3.96) nm; MS m/z (%) = 381 (M$^+$, 100), 253 (5), 191 (8). HRMS calcd for C$_{25}$H$_{19}$NO$_3$ (M$^+$) 381.1365, found 381.1369.

7c: Orange solids, m.p. 248–249ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.34 (s, 2H), 7.84 (d, J = 8.1 Hz, 4H), 7.34 (d, J = 8.1 Hz, 4H), 3.79 (q, J = 7.2 Hz, 2H), 2.44 (s, 6H), 1.31 (t, J = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.2, 148.6, 138.8, 129.9, 127.4, 126.6, 125.5, 121.0, 119.1, 33.2, 21.5, 13.8 ppm; IR (KBr) ν = 1749 (s), 1701 (vs) cm^{-1}; MS m/z (%) = 395 (M$^+$, 100). HRMS Calcd for C$_{26}$H$_{21}$NO$_3$ (M$^+$) 395.1521, found 395.1519.

7d: Reddish orange solids, m.p. 271–273ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.46 (s, 2H), 7.89 (d, J = 8.2 Hz, 4H), 7.39 (dt, J = 8.9, 2.8 Hz, 2H), 7.35 (d, J = 8.2 Hz, 4H), 7.05 (dt, J = 8.9, 2.8 Hz, 2H), 3.89 (s, 3H), 2.45 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.6, 159.3, 148.7, 138.9, 130.0, 127.9, 127.3, 126.1, 125.5, 124.6, 121.0, 119.9, 114.4, 55.5, 21.5 ppm; IR (KBr) ν = 1759 (s), 1712 (vs) cm^{-1}; MS m/z (%) = 473 (M$^+$, 100), 296 (10), 237 (9). HRMS calcd for C$_{31}$H$_{23}$NO$_4$ (M$^+$) 473.1627, found 473.1632.

7e: Orange solids, m.p. 229–232ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.30 (s, 2H), 7.84 (d, J = 8.1 Hz, 4H), 7.33 (d, J = 8.1 Hz, 4H), 4.19 (tt, J = 3.6Hz, 12.3 Hz, 1H), 2.44 (s, 6H) 2.28 (qd, J = 12.3, 3.6 Hz, 2H), 1.89 (d, J = 12.3 Hz, 2H), 1.70–1.77 (m, J =12.3, 3.6 Hz, 3H), 1.27–1.44 (m, J = 12.3, 3.6 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.6, 148.6, 138.9, 130.1, 127.6, 126.7, 125.6, 121.2, 119.0, 51.4, 29.7, 26.2, 25.3, 21.6 ppm; IR (KBr) ν = 1755 (s), 1701 (vs) cm^{-1}; MS m/z (%) = 449 (M$^+$, 100), 367 (28). HRMS Calcd for C$_{30}$H$_{27}$NO$_3$ (M$^+$) 449.1991, found 449.1987.

8a: Reddish orange solids, m.p. 263–264ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.41 (s, 2H), 7.90 (dt, J = 8.9, 2.4 Hz, 4H), 7.53 (t, J = 7.4 Hz, 2H), 7.48 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.07 (dt, J = 8.9, 2.4 Hz, 4H), 3.90 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.4, 160.0, 148.4, 132.0, 129.1, 128.2, 127.1, 126.6, 125.8, 123.0, 120.4, 120.2, 114.8, 55.5 ppm; IR (KBr) ν = 1760 (s), 1707 (vs) cm^{-1}; UV-vis (CH$_3$CN) λ_{max} = 233 (log ε = 4.20), 270 (4.29), 279 (4.36), 308 (4.49), 434 (4.11), 481sh (4.06) nm; MS m/z (%) = 475 (M$^+$, 100), 460 (29), 368 (7), 238 (12), 164 (7), 111 (6), 97 (10), 83 (10), 71 (10). HRMS calcd for C$_{30}$H$_{21}$NO$_5$ (M$^+$) 475.1420, found 475.1420.

8b: Reddish orange solids, m.p. 277–278ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.29 (s, 2H), 7.87 (dt, J = 8.9, 2.5 Hz, 4H), 7.07 (dt, J = 8.9, 2.5 Hz, 4H), 3.90 (s. 6H), 3.22 (s, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.5, 159.9, 148.3, 127.0, 126.2, 123.0, 120.2, 119.2, 114.8, 55.5, 24.3 ppm; IR (KBr) ν = 1756 (vs), 1714 (s) cm^{-1}; MS m/z (%) = 413 (M$^+$, 100), 398 (40), 207 (16). HRMS calcd for C$_{25}$H$_{19}$NO$_5$ (M$^+$) 413.1263, found 413.1263.

8d: Carmine solids, m.p. 230–231ºC. ^{1}HNMR (500 MHz,

CDCl$_3$) δ= 8.38 (s, 2H), 7.88 (dt, *J* = 9.0, 2.4 Hz, 4H), 7.38 (dt, *J* = 8.9, 2.7 Hz, 2H), 7.06 (dtt, *J* = 9.0, 2.4 Hz, 4H), 7.04 (dt, *J* = 8.9, 2.7 Hz, 2H), 3.90 (s, 6H), 3.86 (s, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.6, 160.0, 159.3, 148.4, 127.9, 127.0, 125.8, 124.7, 123.0, 120.4, 120.0, 114.8, 114.4, 55.52, 55.47 ppm; IR (KBr) ν = 1757 (m), 1712 (vs) cm^{-1}; MS *m/z* (%) = 505 (M$^+$, 100), 490 (24), 253 (11). HRMS calcd for C$_{31}$H$_{23}$NO$_6$ (M$^+$) 505.1525, found 505.1520.

2.4. 1,4-diarylnaphthalene-2,3:6,7-bis(dicarboximide)s 18–20

A solution of 1,3-diarylisobenzofuran-5,6-dicarboximide (1.00 mmol) and *N*-substituted maleimide (1.10 mmol) in 10 mL of toluene or dioxane was refluxed on an oil bath under argon atmosphere until the isobenzofuran was consumed completely (5–20 h). Then, the solvent was removed and the residue was purified by SiO$_2$ chromatography to give the Diels-Alder adduct (63–99% yield). This adduct was dissolved in a solution of 10 equivalents of trifluoromethanesulfonic acid in 5 mL of DCE. After being heated at 65ºC for 2 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 NaHCO$_3$ solution and brine, and was dired over Na$_2$SO$_4$. The solvent was removed and the residue was purified by SiO$_2$ chromatography to give the title compound. Two-step yields are shown in Table 3.

18a: Colorless powder, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.30 (s, 2H), 7.61 (m, 6H), 7.42 (m, 4H), 4.04 (tt, *J* = 12.8, 3.4 Hz, 1H), 3.20 (s, 3H), 2.13 (qd, *J* = 12.8, 3.4 Hz, 2H), 1.77 (d, *J* = 12.8 Hz, 2H), 1.64 (d, *J* = 12.8 Hz, 2H), 1.59 (d, *J* = 12.8 Hz, 1H), 1.23 (qt, *J* = 12.8, 3.4 Hz, 2H), 1.13 (qt, *J* = 12.8, 3.4 Hz, 1H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.5, 166.4, 140.8, 138.7, 133.8, 130.1, 129.8, 129.3, 128.7, 126.6, 124.6, 51.6, 29.6, 26.1, 25.1, 24.6 ppm; IR (KBr) ν = 1766 (s), 1718 (vs), 1707 (vs) cm^{-1}; UV (CHCl$_3$) λ_{max} = 251 (log ε = 4.62), 268 (4.77), 315 (4.07), 369 (3.69), 387 (3.88) nm; MS *m/z* (%) = 514 (M$^+$, 66), 433 (100), 415 (6), 301 (7), 276 (11). HRMS calcd for C$_{33}$H$_{26}$N$_2$O$_4$ (M$^+$) 514.1893, found 514.1887.

18b: Creamy white powder, m.p. > 300ºC (sintered above 300ºC). ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.36 (s, 2H), 7.60 (m, 6H), 7.46 (m, 4H), 7.38 (tm, *J* = 7.5 Hz, 2H), 7.35 (dt, *J* = 6.9, 2.0 Hz, 2H), 7.31 (tt, *J* = 6.9, 2.0 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.0, 165.2, 141.6, 138.7, 133.4, 131.3, 130.2, 129.7, 129.2, 128.7, 128.6, 128.1, 126.6, 126.1, 124.5, 33.4, 13.8 ppm; IR (KBr) ν = 1768 (s), 1727 (vs), 1718 (vs), 1711 (s) cm^{-1}; UV (CHCl$_3$) λ_{max} = 248sh (log ε = 4.59), 263 (4.76), 274sh (4.69), 313sh (4.23), 370 (3.71), 388 (3.86) nm; MS *m/z* (%) = 522 (M$^+$, 100), 477 (15), 423 (5), 378 (6), 301 (4), 276 (5). HRMS calcd for C$_{34}$H$_{22}$N$_2$O$_4$ (M$^+$) 522.1580, found 522.1586.

18c: Yellow powder, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.48 (s, 2H), 7.61 (m, 6H), 7.51 (m, 6H), 7.40 (m, 7H), 7.32 (tt, *J* = 6.9, 1.9 Hz, 1H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.1, 165.2, 141.7, 139.0, 133.3, 131.4, 131.3, 129.70, 129.67, 129.3, 129.2, 128.8, 128.7, 128.5, 128.2,

126.6, 126.5, 126.3, 125.3 ppm; IR (KBr) ν = 1772 (s), 1744 (s), 1725 (vs) cm^{-1}; UV (CHCl$_3$) λ_{max} = 259 (log ε=4.68), 288 (4.52), 370 (3.70), 389 (3.82) nm. MS *m/z* (%) = 570 (M$^+$, 100), 525 (14), 378 (9). HRMS calcd for C$_{38}$H$_{22}$N$_2$O$_4$ (M$^+$) 570.1580, found 570.1583.

18d: Yellow microcrystals, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.41 (s, 2H), 7.62 (m, 6H), 7.45 (m, 4H), 7.30 (d, *J* = 9.1 Hz, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 3.84 (s, 3H), 3.66 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.4, 166.1, 159.4, 140.9, 138.7, 133.5, 130.0, 129.6, 129.2, 128.6, 127.8, 126.8, 125.1, 124.0, 114.5, 55.5, 33.3, 13.6 ppm; IR (KBr) ν = 1766 (s), 1732 (s), 1717 (vs), 1706 (s) cm^{-1}; UV (CHCl$_3$) λ_{max} = 263 (log ε = 4.75), 309 (4.25), 369 (3.72), 388 (3.79) nm; MS *m/z* (%) = 552 (M$^+$, 100), 537 (7), 276 (6), 269 (8), HRMS calcd for C$_{35}$H$_{24}$N$_2$O$_5$ (M$^+$) 552.1685, found 552.1687.

19a: Creamy white powder, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.32 (s, 2H), 7.41 (d, *J* = 7.9 Hz, 4H), 7.30 (d, *J* = 7.9 Hz, 4H), 4.05 (tt, *J* = 12.5, 3.5 Hz, 1H), 3.20 (s, 3H), 2.53 (s, 6H), 2.14 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.77 (d, *J* = 12.5 Hz, 2H), 1.64 (d, *J* = 12.5 Hz, 2H), 1.59 (d, *J* = 12.5 Hz, 1H), 1.23 (qt, *J* = 12.5, 3.5 Hz, 2H), 1.12 (qt, *J* = 12.5, 3.5 Hz, 1H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.6, 166.6, 141.0, 139.1, 139.0, 130.7, 129.9, 129.7, 129.5, 126.6, 124.7, 51.5, 29.6, 26.1, 25.2, 24.6, 21.7 ppm; IR (KBr) ν = 1761 (s), 1716 (vs), 1704 (vs) cm^{-1}; UV (CHCl$_3$) λ_{max} = 252 (log ε = 4.60), 268 (4.78), 318sh (3.95), 339sh (3.83), 372 (3.66), 389 (3.81) nm; MS *m/z* (%) = 542 (M$^+$, 95), 461 (100), 445 (11). HRMS Calcd for C$_{35}$H$_{30}$N$_2$O$_4$ (M$^+$) 542.2206, found 542.2202.

19b: Yellow powder, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.38 (s, 2H) 7.29–7.40 (m, 13H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 6H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.2, 165.5, 141.9, 139.2, 139.1, 131.5, 130.6, 130.3, 129.8, 129.5, 128.8, 128.2, 126.7, 126.2, 124.8, 33.6, 21.7, 14.0 ppm; IR (KBr) ν = 1767 (s), 1731 (vs), 1721 (vs) 1717 (s, sh), 1711 (s, sh) cm^{-1}; MS *m/z* (%) = 550 (M$^+$, 100), 535 (28), 505 (11), 491 (6). HRMS Calcd for C$_{36}$H$_{26}$N$_2$O$_4$ (M$^+$) 550.1893, found 550.1893.

19c: Yellow powder, m.p. >300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.51 (s, 2H), 7.52 (tm, *J* = 7.2 Hz, 2H), 7.42 (m, 7H), 7.38 (m, 8H), 7.31 (m, 1H), 2.52 (s, 6H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.4, 165.5, 142.0, 139.4, 139.3, 131.7, 131.5, 130.5, 129.8, 129.7, 129.6, 129.4, 128.9, 128.6, 128.3, 126.72, 126.66, 126.4, 125.6, 21.7 ppm; IR (KBr) ν = 1769 (s), 1748 (s), 1731 (vs), 1721 (vs) cm^{-1}; UV (CHCl$_3$) λ_{max} = 261 (log ε = 4.77), 283 (4.64), 325sh (4.22), 342sh (4.05), 364sh (3.78), 392 (3.82) nm; MS *m/z* (%) = 598 (M$^+$, 100), 583 (19), 553 (9), 406 (5), 299 (7). HRMS Calcd for C$_{40}$H$_{26}$N$_2$O$_4$ (M$^+$) 598.1893 found 598.1901.

19d: Yellow solids, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ= 8.44 (s, 2H), 742 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.31 (dm, *J* = 9.1 Hz, 2H), 7.02 (dm, *J* = 9.1 Hz, 2H), 3.84 (s, 3H), 3.65 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 6H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ= 166.7, 166.4, 159.6, 141.1, 139.2, 139.1, 130.6, 129.8, 129.6, 129.5, 128.0, 126.9, 125.4, 124.2, 114.7, 55.7, 33.4, 21.7, 13.7 ppm; IR (KBr) ν = 1766 (s), 1730 (s), 1716 (vs) 1707 (s) cm^{-1}; UV

(CHCl$_3$) λ_{max} = 264 (log ε = 4.89), 314sh (4.28), 370sh (3.78), 389 (3.83) nm; UV (CH$_3$CN) λ_{max} = 228 (log ε = 4.55), 236 (4.59), 261 (4.84), 302sh (4.31), 367 (3.71), 386 (3.78) nm; MS m/z (%) = 580 (M$^+$, 100), 565 (10), 283 (5). HRMS Calcd for C$_{37}$H$_{28}$N$_2$O$_5$ (M$^+$) 580.1998, found 580.2001.
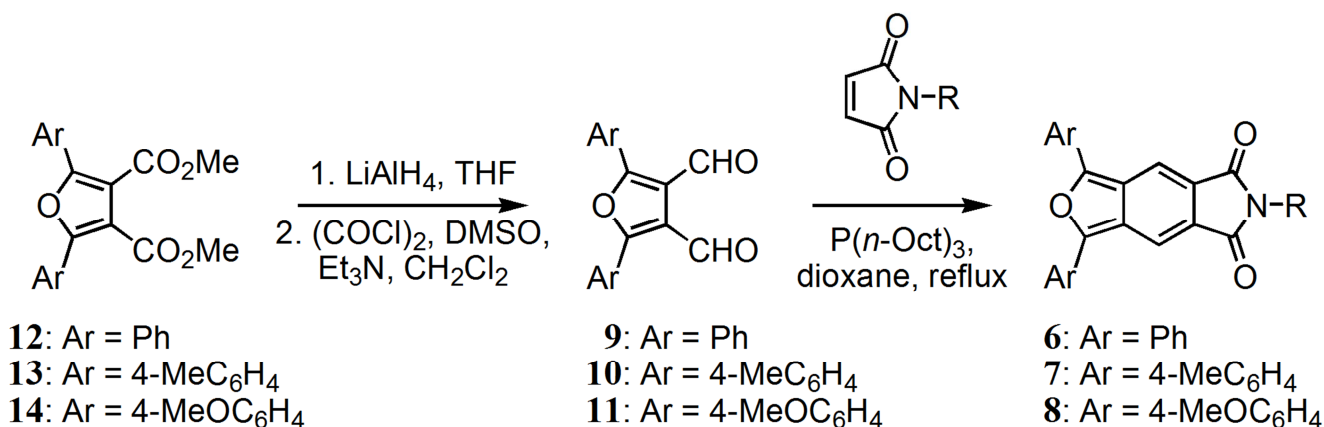
20a: Bright yellow solids, m.p. > 300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.34 (s, 2H), 7.34 (dm, J = 8.8 Hz, 4H), 7.13 (dm, J = 8.8 Hz, 4H), 4.06 (tt, J = 12.5, 3.3 Hz, 1H), 3.95 (s, 6H), 3.21 (s, 3H), 2.15 (qd, J = 12.5, 3.3 Hz, 2H), 1.78 (d, J = 12.5 Hz, 2H), 1.65 (d, J = 12.5 Hz, 2H), 1.60 (d, J = 12.5 Hz, 1H), 1.24 (qt, J = 12.5, 3.3 Hz, 2H), 1.14 (qt, J = 12.5, 3.3 Hz, 1H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 167.4, 166.5, 160.1, 140.5, 139.0, 131.1, 129.8, 126.5, 125.5, 124.6, 114.1, 55.3, 51.4, 29.5, 26.0, 25.0, 24.5 ppm; IR (KBr) ν = 1779m, 1760s, 1716s, 1702vs cm^{-1}; UV (CHCl$_3$) λ_{max} = 250 (log ε = 4.55), 270 (4.76), 300 (3.89), 358 (3.80), 385 (3.69) nm; MS m/z (%) = 574 (M$^+$, 100), 492 (74). HRMS calcd for C$_{35}$H$_{30}$N$_2$O$_6$ (M$^+$) 574.2104, found 574.2111.

20b: Bright yellow solids, m.p. >300ºC. ^{1}HNMR (500 MHz, CDCl$_3$) δ = 8.46 (s, 2H), 7.37 (dm, J = 8.8 Hz, 4H), 7.31 (dm, J = 9.1 Hz, 2H), 7.14 (dm, J = 8.8 Hz, 4H), 7.02 (dm, J = 9.1 Hz, 2H), 3.95 (s, 6H), 3.85 (s, 3H), 3.67 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H) ppm; ^{13}CNMR (126 MHz, CDCl$_3$) δ = 166.6, 166.3, 160.2, 159.4, 140.7, 139.2, 131.2, 129.5, 127.8, 126.6, 125.4, 125.2, 124.1, 114.5, 114.1, 55.5, 55.4, 33.3, 13.6 ppm; IR (KBr) ν = 1765 (s), 1730 (s), 1716 (vs), 1707 (s) cm^{-1}; MS m/z (%) = 612 (M$^+$, 100), 306 (7). HRMS Calcd for C$_{37}$H$_{28}$N$_2$O$_7$ (M$^+$) 612.1897, found 612.1896.

3. Results and Discussion

Furandicarbaldehydes 9–11, prepared from the corresponding dimethyl diesters 12–14 [25] by LiAlH$_4$ reduction and subsequent Swern oxidation, were subjected to the annulation reaction with various N-substituted maleimides to produce the title isobenzofurans 6–8 in a range of 50 to 74% yields (Scheme 2, Table 1). Compounds 6–8 were obtained as slightly air-sensitive orange to red solids.

12: Ar = Ph
13: Ar = 4-MeC$_6$H$_4$
14: Ar = 4-MeOC$_6$H$_4$

9: Ar = Ph
10: Ar = 4-MeC$_6$H$_4$
11: Ar = 4-MeOC$_6$H$_4$

6: Ar = Ph
7: Ar = 4-MeC$_6$H$_4$
8: Ar = 4-MeOC$_6$H$_4$

Scheme 2. Synthesis of 1,3-diarylisobenzofuran-5,6-dicarboximides (6–8).

The UV-vis and emission spectra of 6a–8a are shown in Figure 1. The absorption spectra show mainly two bands around 300 and 450 nm. The latter long wavelength band is very broad, suggesting that it has two excitations. Based on a result of TD-DFT calculations, the band consists of two excitations derived from HOMO –> LUMO and HOMO –> LUMO+1.[26] The spectra of 7a and 8a show a clear red shift and also a hyperchromic effect compared with the spectrum of 6a.

Table 1. Yield of 1,3-diarylisobenzofuran-5,6-dicarboximides (6–8).

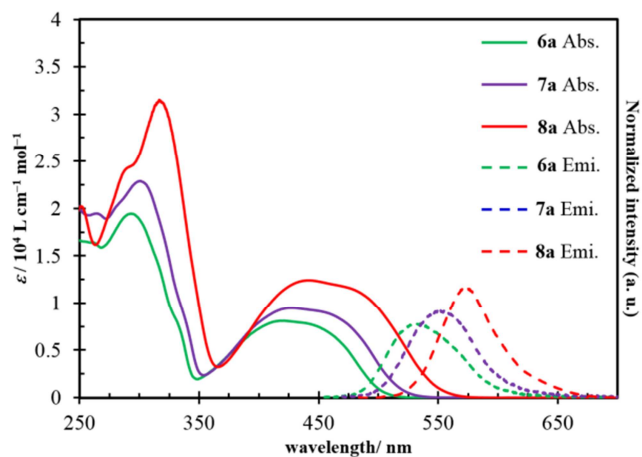| Ar	R	product	Yield (%)
Ph	Ph	6a	68
Ph	Me	6b	67
Ph	Et	6c	74
Ph	4-MeOC$_6$H$_4$	6d	66
4-MeC$_6$H$_4$	Ph	7a	59
4-MeC$_6$H$_4$	Me	7b	63
4-MeC$_6$H$_4$	Et	7c	73
4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	7d	51
4-MeC$_6$H$_4$	c-hex	7e	51
4-MeOC$_6$H$_4$	Ph	8a	50
4-MeOC$_6$H$_4$	Me	8b	70
4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	8d	66

Figure 1. UV-vis absorption (solid line) and emission (broken line) spectra of 6a–8a.
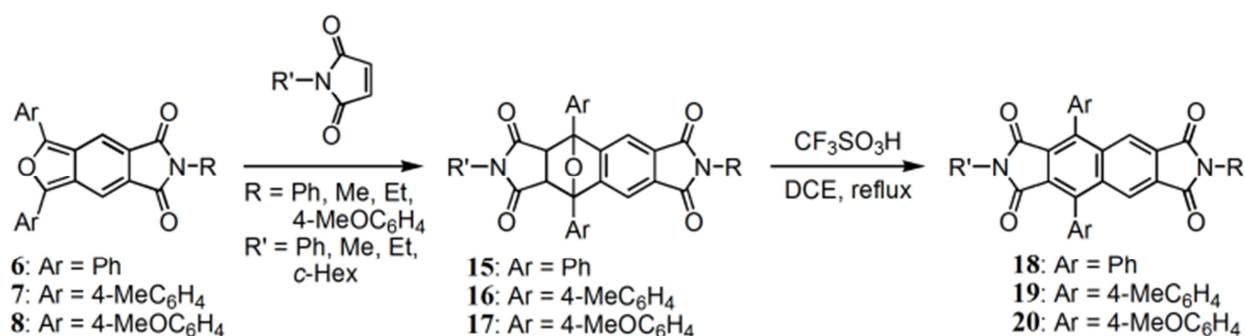
Absorption and emission properties of 6a–8a in acetonitrile are summarized in Table 2. Emission quantum yields were found a range of 1–4%, which are far less than those of 1,3-diphenylisobenzofuran (98%), its 5,6-diester (72%) and

its 5,6-dinitrile (80%) [27–29].

Table 2. *Optical properties of N-phenyl-1,3-diarylisobenzofuran-5,6-dicarboximides (6a–8a) in acetonitrile.*

imides	λ_{abs} / nm	Log ε	λ_{emi} / nm	Stokes shift / nm	Φ / %
6a	419 441sh	3.91 3.89	534	115 93	4
7a	427 460sh	3.98 3.95	552	125 92	2
8a	434 481sh	4.11 4.06	572	138 92	1

Next, compounds 6–8 were employed as an enophile in cycloaddition reaction. The Diels-Alder reaction of 6–8 with

another maleimides and subsequent dehydration with the aid of trifluoromethanesulfonic acid in dichloroethane (DCE) produced naphthalene-2,3:6,7-bis(dicarboximide)s. (Scheme 3) Two-step yields of 18–20 via 15–17 are shown in Table 3. The Diels-Alder reactions were carried out in refluxing toluene or dioxane to give adducts 15–17 in high yields. Dehydration of the adduct 15b (R = Et, R' = Ph) was examined with various acids including HBr, BF$_3$OEt$_2$, Sc(OTf)$_3$, and *p*-toluenesulfonic acid (*p*-TsOH). The best yield was observed under conditions with trifluoromethanesulfonic acid. Naphthalene-2,3:6,7-bis (dicarboximide)s 18–20 were obtained as colorless to yellow solids and their structures were confirmed by spectroscopic analysis.
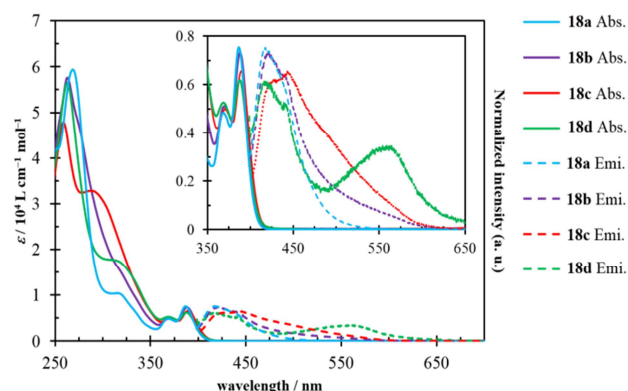

Scheme 3. *Synthesis of naphthalene-2,3:6,7-bis(dicarboximide)s 18–20.*

Table 3. *Results of two-step synthesis of naphthalene-2,3:6,7-bis(dicarboximide)s 18–20 from isobenzofuranimides 6–8.*

Ar	R	R'	product	yield (%)
Ph	Me	*c*-hex	18a	87
Ph	Et	Ph	18b	64
Ph	Ph	Ph	18c	49
Ph	4-MeOC$_6$H$_4$	Et	18d	69
4-MeC$_6$H$_4$	Me	*c*-hex	19a	72
4-MeC$_6$H$_4$	Et	Ph	19b	68
4-MeC$_6$H$_4$	Ph	Ph	19c	81
4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	Et	19d	71
4-MeOC$_6$H$_4$	Me	*c*-hex	20a	84
4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	Et	20b	70

Absorption and emission spectra of 18a–18d and 18a–20a are shown in Figure 2 and 3 and their optical properties are summarized in Table 4. The tailing absorptions of *N*-aryl-substituted bis(dicarboximide)s 18b–d are not depending on their concentrations and hence are thought to be intrinsic dual emission, which has been seen in *N*-phenyl-2,3-naphtalimides [5]. Among them, *N*-*p*-anisyl-*N'*-ethyl derivative 18d showed clearly the dual bands in the emission spectrum. Emission quantum yields were found a range of 0.01–8%. Comparison of the absorption and emission spectra of 18a–20a indicates an effect of the substituents on the phenyl groups at the 1,4-positions of the naphthalene ring. That is, the long-wavelength absorption of 20a is slightly different from those of 18a–19a and the emission maximum shows a red shift depending on electron-donating nature of the substituent on the phenyl rings, indicating possibility to control emission wavelength by the substituent.

Figure 2. *UV-vis absorption (solid line) and emission (broken line) spectra of naphthalene-2,3:6,7-bis(dicarboximide)s 18a–18d.*
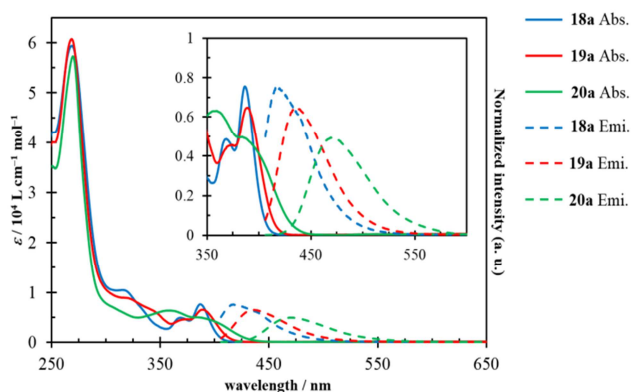

Figure 3. *UV-vis absorption (solid line) and emission (broken line) spectra of naphthalene-2,3:6,7-bis(dicarboximide)s 18a–20a.*

Table 4. *Optical properties of some naphthalene-2,3:6,7-bis(dicarboximide)s 18–20.*

imides	λ_{abs} / nm	log ε	λ_{emi} / nm	Stokes shift / nm	Φ / %
18a	387	3.88	417	30	3
18b	388	3.86	421	33	1
18c	389	3.82	425	36	0.3
			429sh	100	
18d	389	3.88	418	29	0.01
			559	170	
19a	389	3.81	436	47	4
20a	385	3.69	470	85	8

4. Conclusion

We have demonstrated synthesis of the novel isobenzofuran-dicarboximides by phosphine-assisted annulation of 2,5-diarylfuran-3,4-dicarbaldehyde with maleimide. These isobenzofurans were transformed into the corresponding naphthalene-2,3:6,7-bis(dicarboximide)s by the Diels-Alder reaction with another maleimide and subsequent dehydration with the aid of trifluoromethanesulfonic acid. The absorption and emission properties are also described. Further study on synthesis of novel arene-dicarboximides by cycloaddition reaction and subsequent dehydration is now actively in progress.

Acknowledgements

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