Synthesis of novel cyclophanes containing both benzo[1,2-*b*:5,4-*b*′]-difuran and naphthalene rings

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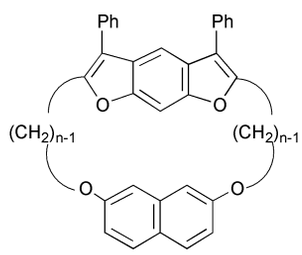
Facile routes for the synthesis of novel cyclophanes **1a**, **b** containing both benzo[1,2-*b*:5,4-*b*′]difuran and naphthalene rings have been developed. Irradiation of 1,5-dibenzoyl-2,4-dialkoxybenzene derivatives **3a**, **b** with a 350 nm mercury lamp followed by dehydration afforded benzo[1,2-*b*:5,4-*b*′]difuran ring systems **5a**, **b**. The cyclophanes **1a**, **b** were prepared either from the ether-forming reaction between the preformed benzodifuran ring derivatives **5a**, **b** and 2,7-dihydroxynaphthalene, or from the photocyclization–dehydration reaction of the macrocycles **6a**, **b** prepared by reacting 1,5-dibenzoyl-2,4-bis(ω-bromoalkoxy)benzene with 2,7-dihydroxynaphthalene. The cyclophanes **2a**, **b** containing two benzo[1,2-*b*:5,4-*b*′]difuran and two naphthalene moieties were obtained as minor products.

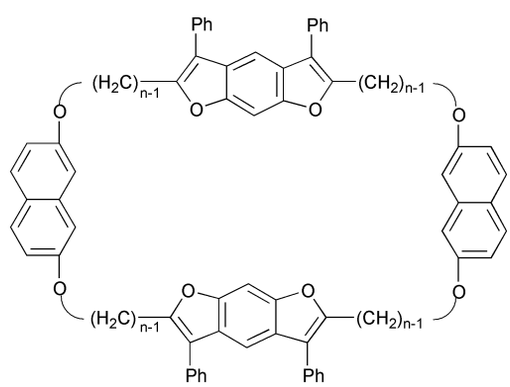
Introduction

The design and synthesis of cyclophanes, macrocycles containing aromatic groups, is a fascinating branch of organic and supramolecular chemistry.[1,2] It is well recognized that cyclophanes have a wide range of applicability in emerging technology as synthetic receptors in molecular recognition, sensors, and components of molecular motors.[2] However, aromatic groups contained in the cyclophanes are mostly carbocyclic rings such as benzene and naphthalene derivatives. Heteroaromatic ring-containing cyclophanes are usually limited to pyrrole- and pyridine-containing systems, presumably due to difficulties in preparing appropriately tethered heterocyclic compounds.

In this paper, we describe facile synthetic routes to novel cyclophanes **1a**, **b** containing both benzo[1,2-*b*:5,4-*b*′]difuran and naphthalene rings. A few groups have reported the synthesis of the benzo[1,2-*b*:5,4-*b*′]difuran nucleus,[3–5] but the benzodifuran ring-containing cyclophanes have not been reported. One reported synthetic method for the benzodifuran rings is based on the formation of furan rings *via* intramolecular aldol-type condensation reactions of the appropriate products, obtained from alkylation of *o*-acylphenols, with the corresponding α-halocarbonyl compound.[3] This method provides only limited scope for the synthesis of benzodifuran derivatives which have specific substituents such as acetyl, cyano, ethoxycarbonyl and carboxy groups at the 2-position. The other methods are for the preparation of 2,3,5,6-tetraarylbenzo[1,2-*b*;5,4-*b*′]difuran derivatives either by a photochemical reaction[4] or by acid-catalyzed cyclocondensation of resorcinol with *p*-(benzyloxy)benzoin.[5] It was shown that *o*-alkoxybenzophenones can be transformed to benzo[*b*]furan rings by photocyclization *via* intramolecular δ-hydrogen abstraction followed by dehydration reactions.[6–8] Here, we have extended this methodology for the formation of the appropriately tethered benzo[1,2-*b*:5,4-*b*′]difuran rings and cyclophanes **1a**, **b**. In the process of preparation of **1a**, **b**, we also obtained the cyclophanes **2a**, **b** containing two benzo[1,2-*b*:5,4-*b*′]difuran and two naphthalene moieties as minor products. The heteroaromatic ring-containing cyclophanes **1** and **2** are of particular interest because of the possibilities of trans-annular excitation energy transfer between the aromatic groups, and cooperative guest binding by sandwiching the guest molecules between the aromatic groups through π–π, electron donor–acceptor, or cation–π interactions.



1a-b



2a-b

a: n=8; **b**: n=12

Results and discussion

For the synthesis of the cyclophanes **1**, we first established a synthetic route to benzo[1,2-*b*:5,4-*b*′]difuran derivatives **5**, starting from 1,3-dimethoxybenzene (Scheme 1). Friedel–Crafts acylation of 1,3-dimethoxybenzene with benzoyl chloride gave 1,5-dibenzoyl-2,4-dihydroxybenzene[4] in 35% yield, which was then reacted with α,ω-dibromoalkanes in a 1 : 5 molar ratio in

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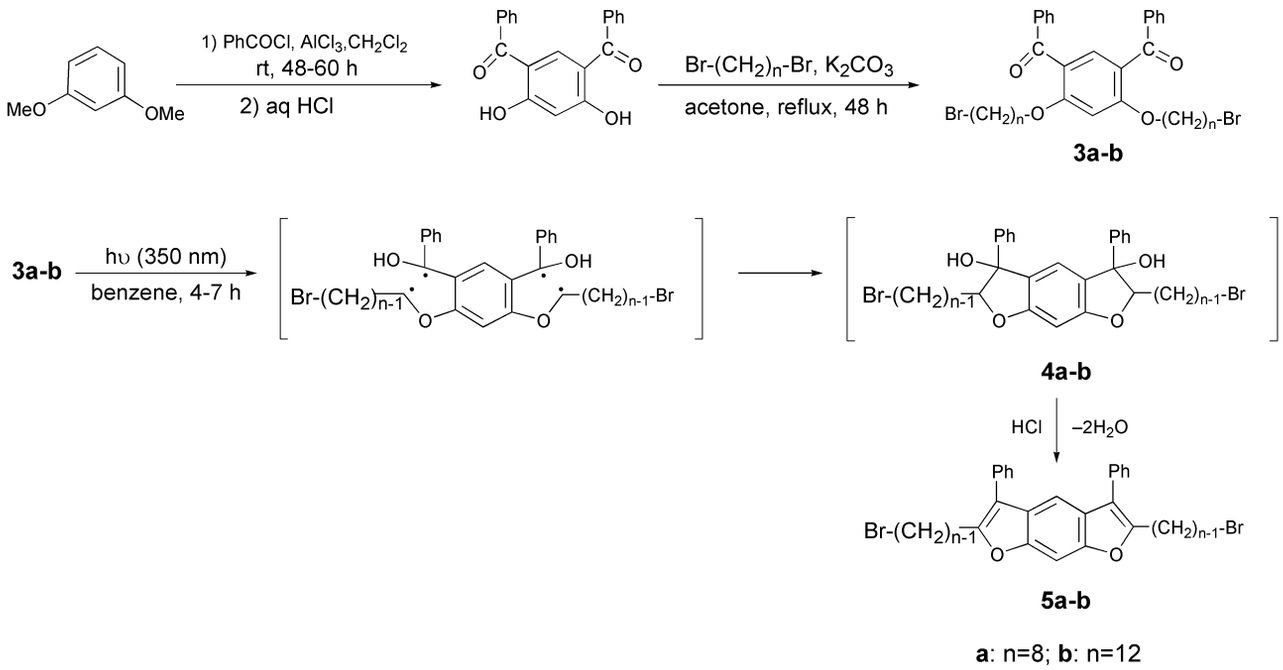


Scheme 1 Synthetic route to benzo[1,2-*b*:5,4-*b*′]difuran derivatives **5**.

the presence of K_2CO_3 to obtain **3a** and **3b** in 66% and 60% yields, respectively. Irradiation of 1.0 mM benzene[9] solutions of compounds **3a**, **b** with 350 nm mercury lamps, followed by dehydration of the photoproducts with aq. HCl, without attempting isolation and separation of the benzodifuranol derivatives **4a**, **b**, afforded benzodifuran derivatives **5a**, **b** in 40% yields.

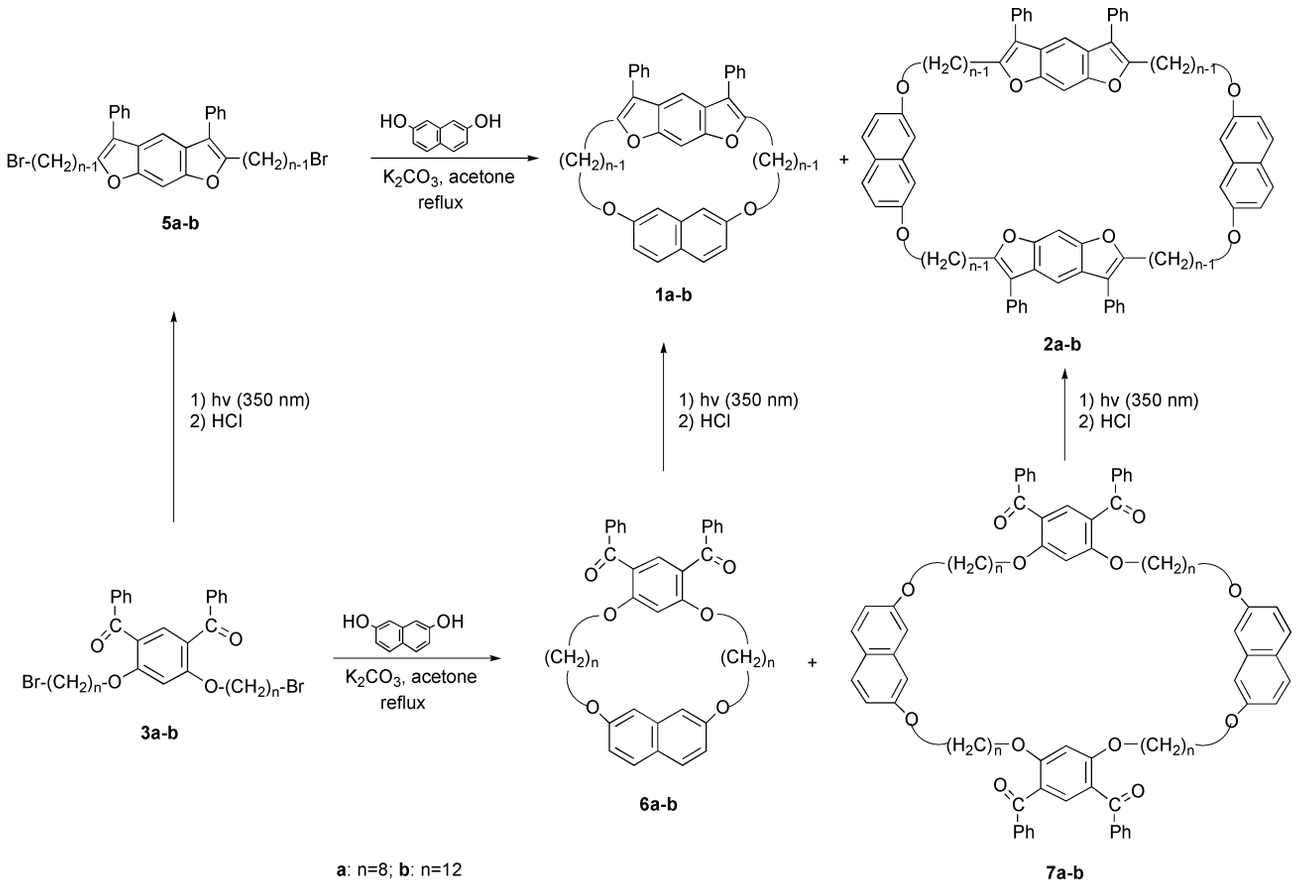
Establishment of a facile synthetic route to 2,6-bis(ω-bromoalkyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b*′]difurans **5a**, **b** prompted us to utilize these compounds in the preparation of benzodifuran ring-containing cyclophanes. The synthetic pathways for the cyclophanes containing both benzodifuran and naphthalene rings, **1a**, **b**, are shown in Scheme 2. The cyclophanes **1a**, **b** were prepared by two alternative routes: one is from the connection of the preformed benzodifuran ring with tethered bromoalkyl groups, **5a**, **b**, with dihydroxynaphthalene through formation of two ether linkages. The other is the reverse order of the first one; the aforementioned photocyclization reaction to form the benzodifuran ring was applied to macrocycles **6a**, **b**, which were obtained by the ether-forming reaction between dibromides **3a**, **b** and dihydroxynaphthalene.

The ether-forming reactions of 2,7-dihydroxynaphthalene with **5a**, **b** provided **1a**, **b** in 34–37% yields, together with the cyclophanes containing two benzodifuran rings and two naphthalene rings, **2a**, **b** in 10–13% yields. The reactions of **3a**, **b** with 2,7-dihydroxynaphthalene gave **6a**, **b** in 33–37% yields and the [2 + 2] products **7a**, **b** in 11% yields. Photocyclization reactions of the macrocycles **6a**, **b** and then dehydration reactions of the photoproducts gave **1a** and **1b** in 34% and 36% yields, respectively. These results show that the overall yields for the cyclophanes **1a**, **b** starting from **3a**, **b** are almost the same for both routes. This scheme provides facile access to rather complex molecules such as **1a**, **b** from readily available and straightforward experimental procedures.

The cyclophanes **2a**, **b** were also obtained *via* the photocyclization–dehydration reaction of **7a**, **b** with yields of 10–14%; in this case, the overall yields from **3a**, **b** to **2a**, **b** are much higher for the route *via* **5a**, **b** than for the route *via* **7a**, **b**. This is expected as the latter route requires a quadruple photocyclization step involving simultaneous formation of four furan rings, while the former route contains a double photocyclization step.

The structures of the compounds prepared in this work were fully characterized by ^{1}H and ^{13}C NMR spectra and elemental analysis. The number of ^{1}H and ^{13}C NMR peaks confirmed the symmetrical nature of the compounds. Based on the symmetry of the compounds, the expected number of ^{13}C NMR peaks is the same among the corresponding macrocycles **1**, **2**, **6**, and **7**, which is 23 for the **a** series and 27 for the **b** series. The actual carbon numbers present in the compounds are 46 for **1a** and **6a**, 54 for **1b** and **6b**, 92 for **2a** and **7a**, and 108 for **2b** and **7b**. The observed number of peaks in the ^{13}C NMR spectra exactly match the expected number, except that **1b** and **7b** have one less peak, and **2b** and **5b** have two less peaks than expected because of overlapping of some alkyl carbons. Of course, the syntheses of the cyclophanes **1a**, **b** and **2a**, **b** *via* two alternative routes constitute further firm evidence of their structures.

In summary, facile routes for the synthesis of novel types of cyclophanes **1a**, **b** having both benzo[1,2-*b*:5,4-*b*′]difuran and naphthalene rings have been developed. The benzodifuran moieties were formed by photocyclization–dehydration reactions of 2,4-dialkoxy substituted 1,5-dibenzoylbenzene derivatives. The cyclophanes **1a**, **b** were prepared either from the reaction of the preformed benzodifuran ring derivatives **5a**, **b** with 2,7-dihydroxynaphthalene or from the photo-reaction of the macrocycles **6a**, **b** having a 1,5-dibenzoyl-2,4-dialkoxybenzene moiety and a naphthalene ring. The cyclophanes **2a**, **b** containing two benzo[1,2-*b*:5,4-*b*′]difuran rings and two naphthalene rings were also obtained as minor products. The cyclophanes **1** and **2** are of particular interest as aryl substituted benzo[1,2-*b*:5,4-*b*′]difuran derivatives have high fluorescence quantum yields,[4] and the close proximity of naphthyl groups to benzodifuran rings in the cyclophanes may facilitate the intramolecular excitation energy transfer. Indeed, the shape of the fluorescence spectra of **1a**, **b** is observed to be essentially the same as that of 2,7-dimethoxynaphthalene, but the emission intensity of **1a**, **b** is much greater than that of 2,7-dimethoxynaphthalene.[10] This indicates efficient excitation energy transfer from benzodifuran to naphthyl groups in the macrocycles. The use of these cyclophanes as fluorescent receptors and components of photochemical molecular devices looks promising. The schemes described here can be easily applied to the syntheses of various other types of benzodifuran ring-containing cyclophanes having different tethering groups, different aromatic rings with specific substituents, and other components rather than naphthalene rings to tune their physicochemical properties for desired applications.



Scheme 2 Synthesis of the cyclophanes containing both benzodifuran rings and naphthalene rings.

Experimental

All reagents were purchased from Aldrich Chemical Co. and used as received. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, using tetramethylsilane as an internal standard in $CDCl_3$. NMR measurements and elemental analyses were performed at the Central Research Facilities of Chungnam National University.

1,5-Dibenzoyl-2,4-dihydroxybenzene

The reported procedure[4] was followed using 1,3-dimethoxybenzene (13.8 g, 0.1 mol), benzoyl chloride (30.9 g, 0.22 mol), and $AlCl_3$ (29.3 g, 0.22 mol) in dichloromethane (250 ml) to give the title compound (11.2 g, 35%); mp 151–153 °C (lit.,[4] 147–149 °C); ^{1}H NMR δ 6.62 (s, 1H, Ar-*H ortho* to both OH groups), 7.3–7.7 (m, 10H), 8.01 (s, 1H, Ar-*H ortho* to both carbonyl groups), 12.86 (s, 2H, two -OH).

1,5-Dibenzoyl-2,4-dialkoxybenzenes 3a, b

A solution of 1,8-dibromooctane (12.8 g, 47.1 mmol) or 1,12-dibromododecane (15.5 g, 47.1 mmol) in acetone (80 ml) was added very slowly to the suspension of 1,5-dibenzoyl-2,4-dihydroxybenzene (3.00 g, 9.42 mmol) and K_2CO_3 (6.51 g, 47.1 mmol) in acetone (100 ml) at reflux which was continued for 48 h. K_2CO_3 was removed by filtration. Water (50 ml) was added to the concentrated filtrate and extracted with dichloromethane. Purification of the organic layer by silica gel column chromatography (eluent: dichloromethane) gave **3a**, **b**.

3a. Yield, 66%; mp 87–88 °C; ^{1}H NMR δ 1.0–1.5 (m, 20H), 1.82 (quintet, J = 7 Hz, 4H), 3.40 (t, J = 7 Hz, 4H, two -CH_2-Br), 3.92 (t, J = 6 Hz, 4H, two -CH_2O-), 6.46 (s, 1H, Ar-*H ortho* to both alkoxy groups), 7.41 (t, J = 8 Hz, 4H, *meta* Ar-*H* of two C_6H_5CO-), 7.52 (tt, J = 8 & 1 Hz, 2H, *para* Ar-*H* of two C_6H_5CO-), 7.68 (s, 1H, Ar-*H ortho* to both benzoyl groups), 7.75–7.78 (m, 4H, *ortho* Ar-*H* of C_6H_5CO-); ^{13}C NMR δ 25.45, 27.93, 28.40, 28.65, 28.89, 32.65, 33.97, 68.50, 96.15, 121.02, 128.01, 129.33, 132.33, 133.31, 138.89, 161.27, 195.22.

3b. Yield, 60%; mp 82–83 °C; ^{1}H NMR δ 1.0–1.5 (m, 36H), 1.86 (quintet, J = 7 Hz, 4H), 3.41 (t, J = 7 Hz, 4H, two -CH_2-Br), 3.92 (t, J = 6 Hz, 4H, two -CH_2O-), 6.45 (s, 1H, Ar-*H ortho* to both alkoxy groups), 7.41 (t, J = 8 Hz, 4H, *m-H* of two C_6H_5CO-), 7.52 (tt, J = 8 & 1 Hz, 2H, *p-H* of two C_6H_5CO-), 7.68 (s, 1H, Ar-*H ortho* to both benzoyl groups), 7.75–7.78 (m, 4H, *o-H* of two C_6H_5CO-); ^{13}C NMR δ 25.82, 25.92, 28.35, 28.95, 29.37, 29.55, 29.60, 29.67, 29.75, 33.02, 34.24, 68.87, 96.50, 121.34, 128.24, 129.58, 132.54, 133.55, 139.19, 161.56, 195.47.

Photocyclization–dehydration reactions of 3a, b to 5a, b

1.0 mM Benzene[9] solutions (500 ml) of compounds **3a**, **b** (0.5 mmol) contained in a Pyrex glass vessel were purged with nitrogen for 1 h and then irradiated under nitrogen with a 350 nm mercury lamp using a RPR-100 photochemical reactor (Southern New England Ultraviolet Company). After 4–7 h of irradiation, the reaction mixture was concentrated and the residue was dissolved in 5 ml of acetone. The acetone solution was treated with a few drops of 1 M HCl and stirred for 2 h. Water was added to the reaction mixture, and extracted with chloroform. The concentrated organic layer was purified by silica gel column chromatography eluting with 1 : 1 hexane–dichloromethane to afford benzodifuran derivatives **5a**, **b**.

5a. Yield, 40%; mp 86–87 °C; ^{1}H NMR δ 1.25–1.43 (m, 12H, two -CH_2CH_2-(CH_2)$_3$-CH_2CH_2Br), 1.75–1.84 (m, 8H, two -CH_2CH_2-(CH_2)$_3$-CH_2CH_2Br), 2.84 (t, J = 8 Hz, 4H, two

furan-CH_2-$(CH_2)_6$Br), 3.36 (t, J = 7 Hz, 4H, two -CH_2-Br), 7.32–7.38 (m, 2H, *p-H* of two C_6H_5), 7.43–7.49 (m, 8H, *o-* & *m-H* of two C_6H_5), 7.55 and 7.54 (2s, 2H, H^4 & H^8 of benzodifuran ring); ^{13}C NMR δ 26.70, 27.99, 28.16, 28.36, 28.94, 32.68, 33.92, 93.63, 107.91, 116.97, 125.44, 126.95, 128.76, 129.13, 133.03, 152.04, 155.06. Anal. Calcd. for $C_{36}H_{40}Br_2O_2$: C, 65.07; H, 6.07%. Found: C, 64.81; H, 5.93%.

5b. Yield, 39%; mp 41–42 °C; ^{1}H NMR δ 1.20–1.44 (m, 28H, two -CH_2CH_2-$(CH_2)_7$-CH_2CH_2Br), 1.74–1.87 (m, 8H, two -CH_2CH_2-$(CH_2)_7$-CH_2CH_2Br), 2.83 (t, J = 8 Hz, 4H, two furan-CH_2-$(CH_2)_{10}$Br), 3.38 (t, J = 7 Hz, 4H, two -CH_2-Br), 7.31–7.37 (m, 2H, *p-H* of two C_6H_5), 7.42–7.49 (m, 8H, *o-* & *m-H* of two C_6H_5), 7.55 (s, 2H, H^4 & H^8 of benzodifuran ring); ^{13}C NMR δ 26.80, 28.10, 28.30, 28.68, 29.20, 29.33, 29.39, 32.77, 33.91, 93.57, 107.84, 116.57, 125.41, 126.85, 128.68, 129.10, 133.06, 152.01, 155.22. Anal. Calcd. for $C_{44}H_{56}Br_2O_2$: C, 68.04; H, 7.27%. Found: C, 67.79; H, 7.13%.

Synthesis of 1a, b and 2a, b from 5a, b

The compound **5a**, **b** (0.30 mmol) was reacted with 2,7-dihydroxynaphthalene (58 mg, 0.36 mmol) in refluxing acetone (50 ml) in the presence of K_2CO_3 (0.42 g, 3.0 mmol) for 48–72 h and worked-up as described for the synthesis of **3a**, **b**. Silica gel column chromatography eluting with 1 : 1 hexane–dichloromethane afforded **1a**, **b** and **2a**, **b** as separate fractions.

1a. Yield, 34%; mp 91–92 °C; ^{1}H NMR δ 1.25–1.45 (m, 12H, two -$(CH_2)_2(CH_2)_3(CH_2)_2$O-), 1.70–1.85 (m, 8H, two furan-$CH_2CH_2(CH_2)_3CH_2CH_2$O-), 2.88 (t, J = 6 Hz, 4H, two furan-CH_2-), 4.00 (t, J = 7 Hz, 4H, two -CH_2O-), 6.95 (dd, J = 9 & 2 Hz, 2H, H^3 & H^6 of naphthalene ring), 7.04 (d, J = 2 Hz, 2H, H^1 & H^8 of naphthalene ring), 7.32–7.38 (m, 2H, *p-H* of two C_6H_5-), 7.43–7.50 (m, 8H, *o-* & *m-H* of two C_6H_5-), 7.58 and 7.63 (2s, 2H, H^4 & H^8 of benzodifuran ring), 7.61 (d, J = 9 Hz, 2H, H^4 & H^5 of naphthalene ring); ^{13}C NMR δ 25.52, 26.37, 27.78, 28.35, 28.58, 29.02, 68.02, 93.93, 106.53, 107.89, 115.98, 117.31, 124.10, 125.55, 126.97, 128.78, 128.94, 129.18, 132.96, 135.94, 152.02, 155.22, 157.39. Anal. Calcd. for $C_{46}H_{46}O_4$: C, 83.35; H, 6.99%. Found: C, 83.38; H, 6.73%.

2a. Yield, 13%; mp 199–200 °C; ^{1}H NMR δ 1.33–1.50 (m, 24H, -$(CH_2)_2(CH_2)_3(CH_2)_2$O-), 1.79 (m, 16H, -$CH_2CH_2(CH_2)_3CH_2CH_2$O-), 2.85 (t, J = 7 Hz, 8H, furan-CH_2-), 4.01 (t, J = 7 Hz, 8H, -CH_2O-), 6.95 (dd, J = 9 & 3 Hz, 4H, H^3 & H^6 of naphthalene ring), 7.01 (d, J = 2 Hz, 4H, H^1 & H^8 of naphthalene ring), 7.31–7.36 (m, 4H, *p-H* of C_6H_5-), 7.42–7.49 (m, 16H, *o-* & *m-H* of C_6H_5-), 7.54 and 7.55 (2s, 2H, H^4 & H^8 of benzodifuran ring), 7.61 (d, J = 9 Hz, 4H, H^4 & H^5 of naphthalene ring); ^{13}C NMR δ 25.78, 26.74, 28.13, 28.91, 28.99, 29.03, 67.80, 93.65, 106.00, 107.92, 116.24, 116.75, 124.11, 125.47, 126.94, 128.75, 129.00, 129.16, 133.07, 135.93, 152.05, 155.17, 157.57. Anal. Calcd. for $C_{92}H_{92}O_8$: C, 83.35; H, 6.99%. Found: C, 83.37; H, 6.91%.

1b. Yield, 37%; mp 158–159 °C; ^{1}H NMR δ 1.20–1.50 (m, 28H, two -$(CH_2)_2(CH_2)_7(CH_2)_2$O-), 1.73–1.85 (m, 8H, two furan-$CH_2CH_2(CH_2)_7CH_2CH_2$O-), 2.85 (t, J = 7 Hz, 4H, two furan-CH_2-), 4.06 (t, J = 7 Hz, 4H, two -CH_2O-), 6.96 (dd, J = 9 & 2 Hz, 2H, H^3 & H^6 of naphthalene ring), 7.04 (d, J = 2 Hz, 2H, H^1 & H^8 of naphthalene ring), 7.32–7.37 (m, 2H, *p-H* of two C_6H_5-), 7.42–7.49 (m, 8H, *o-* & *m-H* of two C_6H_5-), 7.55 and 7.57 (2s, 2H, H^4 & H^8 of benzodifuran ring), 7.61 (d, J = 9 Hz, 2H, H^4 & H^5 of naphthalene ring); ^{13}C NMR δ 25.75, 26.64, 28.03, 28.68, 28.79, 28.96, 29.06, 29.15, 29.28, 67.87, 93.64, 106.28, 107.89, 116.15, 116.82, 124.13, 125.47, 126.91, 128.74, 128.99, 129.17, 133.09, 135.96, 152.04, 155.30, 157.51. Anal. Calcd. for $C_{54}H_{62}O_4$: C, 83.68; H, 8.06%. Found: C, 83.35; H, 8.33%.

2b. Yield, 10%; mp 122–124 °C; ^{1}H NMR δ 1.20–1.50 (m, 56H, -$(CH_2)_2(CH_2)_7(CH_2)_2$O-), 1.73–1.85 (m, 16H, -CH_2CH_2-$(CH_2)_7CH_2CH_2$O-), 2.83 (t, J = 7 Hz, 8H, furan-CH_2-), 4.03 (t, J = 7 Hz, 8H, -CH_2O-), 6.96 (dd, J = 9 & 2 Hz, 4H, H^3 & H^6 of naphthalene ring), 7.01 (d, J = 3 Hz, 4H, H^1 & H^8 of naphthalene ring), 7.31–7.36 (m, 4H, *p-H* of C_6H_5-), 7.41–7.48 (m, 16H, *o-* & *m-H* of C_6H_5-), 7.54 and 7.55 (2s, 2H, H^4 & H^8 of benzodifuran ring), 7.61 (d, J = 9 Hz, 4H, H^4 & H^5 of naphthalene ring); ^{13}C NMR δ 25.96, 26.81, 28.24, 29.14, 29.24, 29.34, 29.39, 29.43, 67.89, 93.62, 105.98, 107.87, 116.25, 116.64, 124.09, 125.45, 126.88, 128.73, 129.00, 129.17, 133.10, 135.96, 152.04, 155.31, 157.62. Anal. Calcd. for $C_{108}H_{124}O_8$: C, 83.68; H, 8.06%. Found: C, 83.54; H, 8.19%.

Synthesis of 6a, b and 7a, b

The reaction of **3a** (1.00 g, 1.43 mmol) or **3b** (1.00 g, 1.23 mmol) with 2,7-dihydroxynaphthalene (1.2 equiv.) was carried out in the same manner as the corresponding reaction of **5a**, **b**. Purification of the reaction mixture by silica gel column chromatography eluting with 40 : 1 dichloromethane–ethyl acetate provided **6a**, **b** and **7a**, **b** as separate fractions.

6a. Yield, 33%; mp 169 °C; ^{1}H NMR δ 1.15–1.52 (m, 20H), 1.81 (quintet, J = 7 Hz, 4H), 3.93 (t, J = 7 Hz, 4H), 4.12 (t, J = 7 Hz, 4H), 6.50 (s, 1H, Ar-*H ortho* to both alkoxy groups), 6.98 (dd, J = 9 & 2 Hz, 2H, H^3 & H^6 of naphthalene ring), 7.05 (d, J = 2 Hz, 2H, H^1 & H^8 of naphthalene ring), 7.40 (t, J = 8 Hz, 4H, *m-H* of two C_6H_5CO-), 7.51 (t, J = 8 Hz, 2H, *p-H* of two C_6H_5CO-), 7.64 (d, J = 9 Hz, 2H, H^4 & H^5 of naphthalene ring), 7.66 (s, 1H, Ar-*H ortho* to both benzoyl groups), 7.76 (d, J = 9 Hz, 4H, *o-H* of two C_6H_5CO-); ^{13}C NMR δ 25.02, 25.36, 27.99, 28.23, 28.27, 28.54, 67.72, 68.54, 96.81, 106.56, 116.06, 121.11, 124.13, 128.03, 129.13, 129.38, 132.36, 133.35, 135.79, 138.84, 157.35, 161.29, 195.13.

7a. Yield, 11%; mp 180–181 °C; ^{1}H NMR δ 1.01–1.53 (m, 40H), 1.80 (broad s, 8H), 3.91 (broad s, 8H), 4.04 (broad s, 8H), 6.45 (s, 2H, Ar-*H ortho* to both alkoxy groups), 6.98 (d, J = 9 Hz, 4H, H^3 & H^6 of naphthalene rings), 7.04 (s, 4H, H^1 & H^8 of naphthalene rings), 7.39 (t, J = 7 Hz, 8H, *m-H* of C_6H_5CO-), 7.50 (t, J = 7 Hz, 4H, *p-H* of C_6H_5CO-), 7.63 (d, J = 9 Hz, 4H, H^4 & H^5 of naphthalene rings), 7.67 (s, 2H, Ar-*H ortho* to both benzoyl groups), 7.75 (d, J = 7 Hz, 8H, *o-H* of C_6H_5CO-); ^{13}C NMR δ 25.32, 25.79, 28.54, 28.87, 28.91, 29.04, 67.76, 68.50, 96.34, 105.97, 116.18, 121.11, 124.12, 128.03, 129.05, 129.37, 132.35, 133.30, 135.93, 138.91, 157.59, 161.28, 195.20. Anal. Calcd. for $C_{92}H_{100}O_{12}$: C, 79.05; H, 7.21%. Found: C, 78.70; H, 7.31%.

6b. Yield, 37%; mp 118–119 °C; ^{1}H NMR δ 1.05–1.52 (m, 36H), 1.84 (quintet, J = 7 Hz, 4H), 3.91 (t, J = 7 Hz, 4H), 4.08 (t, J = 7 Hz, 4H), 6.46 (s, 1H, Ar-*H ortho* to both alkoxy groups), 6.98 (dd, J = 9 & 2 Hz, 2H, H^3 & H^6 of naphthalene ring), 7.03 (d, J = 2 Hz, 2H, H^1 & H^8 of naphthalene ring), 7.40 (t, J = 8 Hz, 4H, *m-H* of two C_6H_5CO-), 7.51 (t, J = 8 Hz, 2H, *p-H* of two C_6H_5CO-), 7.63 (d, J = 9 Hz, 2H, H^4 & H^5 of naphthalene ring), 7.66 (s, 1H, Ar-*H ortho* to both benzoyl groups), 7.74–7.77 (m, 4H, *o*-H of two C_6H_5CO-); ^{13}C NMR δ 25.22, 25.66, 28.33, 28.56, 28.68, 28.75, 29.05, 29.11, 29.13, 29.28, 67.74, 68.50, 96.44, 106.13, 116.15, 121.04, 124.08, 128.02, 129.05, 129.37, 132.36, 133.39, 135.86, 138.87, 157.49, 161.29, 195.20.

7b. Yield, 11%; mp 146–147 °C; ^{1}H NMR δ 1.01–1.52 (m, 72H), 1.83 (quintet, J = 7 Hz, 8H), 3.90 (t, J = 6 Hz, 8H), 4.05 (t, J = 7 Hz, 8H), 6.45 (s, 2H, Ar-*H ortho* to both alkoxy groups), 6.97 (dd, J = 9 & 2 Hz, 4H, H^3 & H^6 of naphthalene rings), 7.02 (s, 4H, H^1 & H^8 of naphthalene rings), 7.40 (t, J = 7 Hz, 8H, *m-H* of C_6H_5CO-), 7.51 (t, J = 7 Hz, 4H, *p-H* of C_6H_5CO-), 7.62 (d, J = 9 Hz, 4H, H^4 & H^5 of naphthalene rings), 7.68 (s,

2H, Ar-*H ortho* to both benzoyl groups), 7.75 (d, J = 7Hz, 8H, *o*-*H* of C_6H_5CO-); ^{13}C NMR δ 25.46, 25.98, 28.60, 29.01, 29.15, 29.26, 29.38, 29.41, 29.45, 67.87, 68.59, 96.30, 105.97, 116.20, 121.09, 124.09, 128.02, 128.99, 129.35, 132.33, 133.33, 135.93, 138.95, 157.60, 161.31, 195.24. Anal. Calcd. for $C_{108}H_{132}O_{12}$: C, 79.96; H, 8.20%. Found: C, 79.86; H, 8.56%.

Photocyclization–dehydration reactions of macrocycles 6a, b and 7a, b

These were carried out in the same way as described for the reactions of **3a**, **b**. The macrocycles **6a**, **b** provided **1a** and **1b** with 34% and 36% yields, and **7a**, **b** gave **2a** and **2b** in 14% and 10% yields, respectively.

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References and notes

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9 Benzene is a toxic solvent and should be handled with appropriate care.
10 The absorption maxima and molar absorptivity (in M^{-1} cm^{-1}) of **5a**, **b** in acetonitrile solvent are 273 (ε = 16200), 302 (13000), 308 (12500) and 315 (12700) nm, whereas those of 2,7-dimethoxynaphthalene (DMN) are 275 (ε = 3400), 310 (2100), 316 (1700), and 325 (3000) nm. The absorption spectra of **1a**,**b** are almost identical with 1 : 1 mixtures of **5a**, **b** and DMN, suggesting little interaction between the aromatic groups in the cyclophanes. The emission spectra of **5a**, **b** as well as 1 : 1 mixtures of **5a**, **b** and DMN were observed as a single band with the long wavelength limit of 311 nm: because of low molar absorptivity of DMN, it appears that the naphthalene fluorescence contributes little to the spectra of the mixtures. The shape of emission spectra of **1a**,**b** was virtually identical to that of DMN showing a peak at 342 nm and a shoulder at *ca.* 330 nm, but the emission intensity of **1a**,**b** was 5.4 times greater than that of DMN at the same concentration. This indicates that the efficiency of the excitation energy transfer from the benzodifuran to the naphthalene moiety is almost 100%. The energy transfer seems to be facilitated by overlapping of the emission band of the benzodifuran moiety with the 325 nm absorption band of the naphthalene moiety.