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Porphyrin molecular tweezers for fullerenes

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Dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday

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ABSTRACT: Facing zinc bisporphyrins connected with diethanoanthracene and diethanonaphthacene (*syn*-**1** and *syn*-**2**) are prepared by double [3+1] porphyrin synthesis of tripyrranedicarbaldehyde with *syn*-5,11-dimethoxy-4,6,10,12-tetrahydro-4,12;6,10-diethanoanthracene[2,3-*c*;7,8-*c′*]dipyrrole and *syn*-4,7,11,14-tetrahydro-4,14;7,11-diethanonaphthacene[2,3-*c*;8,9-*c′*]dipyrrole. These bisporphyrins contain large clefts with different sizes capable for complexation with fullerenes such as C_{60} and C_{70}. These designed *syn*-oriented bisporphyrins serve as effective and selective molecular tweezers for C_{70}. Binding affinity of the zinc bisporphyrins, namely, *syn*-**1** and *syn*-**2**, towards C_{60} and C_{70} in solution is determined by employing UV-vis spectrophotometric technique. Values of binding constants (K) in toluene for the non-covalent complexes of *syn*-**1** with C_{60} and C_{70} are estimated to be $3.1(4) \times 10^4$ and $5.0(2) \times 10^5$ M^{-1}, respectively, and those of *syn*-**2** with C_{60} and C_{70} are enumerated to be $2.1(4) \times 10^4$ and $1.70(13) \times 10^5$ M^{-1}, respectively. Binding of C_{60} and C_{70} in the clefts of *syn*-**1** and *syn*-**2** is clearly demonstrated by the crystal structures of C_{60}/*syn*-**1**, C_{70}/*syn*-**1**, C_{60}/*syn*-**2**, and C_{70}/*syn*-**2** complexes. In the crystal structures with C_{70}, the directions of the long axis of C_{70} are found to be quite different: in the case of C_{70}/*syn*-**1** complex the axis lies perpendicularly to the line connecting two zinc atoms; however, for the C_{70}/*syn*-**2** complex, the axis occupies in-plane to the same line. Both the clefts of *syn*-**1** and *syn*-**2** are induced to fit the included fullerenes by domed out-of-plane distortion of porphyrin rings. Moreover, the bicyclo[2.2.2]octadiene moieties of *syn*-**1** are widened by complexation with the fullerenes, while the same moieties of *syn*-**2** are narrowed by the complexation. Therefore, *syn*-**1** catches the fullerenes at the shallow part of the cleft. On the other hand, *syn*-**2** catches the fullerenes at the bottom part of the cleft. NMR experiments of the complexes in THF-d_8 also support these orientations even in solution.

KEYWORDS: molecular tweezers, fullerenes, bisporphyrin, crystal structure, binding affinity.

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INTRODUCTION

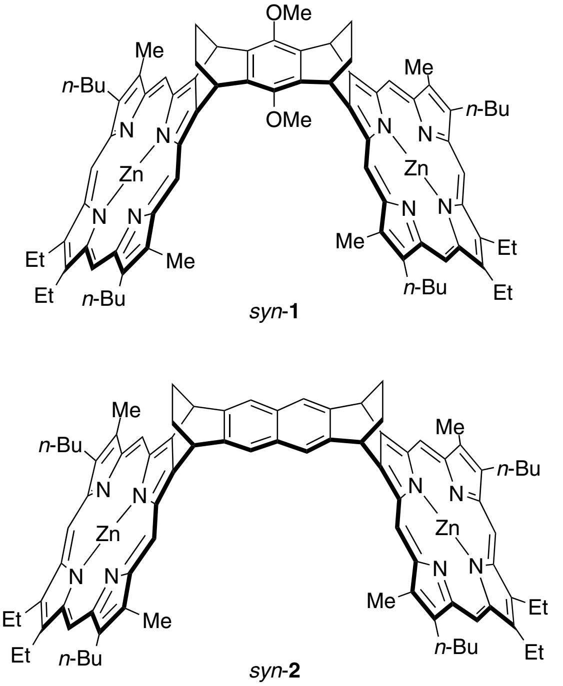
There is great interest among scientists in carbon materials such as fullerenes, graphenes, and carbon nanotubes due to their applicability to nano devices with high performance [1]. These materials, however, are rather hard to deal with for chemists because they are usually handled not as discrete molecules but as bulk substances. Many chemists pay attention to separation and isolation of these materials with a purely discrete molecular composition. One of the main problems for bulk preparation of these materials is their poor solubility which prevents chemists from using common purification methods. Much effort has been made to solubilize these materials, which was followed by successful results based on utilization of weak π–π interactions have been reported [2]. Even now, however, fullerenes with low molecular weights such as C_{60} and C_{70} are the only such compounds that are available as discreet molecular materials with single composition. We planned to isolate these materials with uniform molecular composition and started to prepare the compounds bearing a large cleft which may recognize the carbon materials bearing a curved surface such as fullerenes and carbon nanotubes.

For this purpose, we have focused our attention on the work of molecular tweezers and clips developed by Klärner and his coworkers [3]. They have used *syn*-oriented oligomethanoacenes as molecular tweezers for electron-defficient aromatic compounds such as nitrated benzenes, cyanated benzenes, and pyridinium compounds. It is also reported that fullerene and porphyrin form naturally assembled co-crystallates, which are characterized by an unusually short distance of fullerene/porphyrin (3.0–3.5 Å) [4] and that a number of fullerene/porphyrin systems form an emissive charge transfer (CT) state both in solutions [5] and in solid state [6]. These systems differ from previously studied emitting CT systems by the size of interacting electron subsystems, which are significantly larger as compared to anthracene derivatives [7]. We anticipated that the designed molecular tweezers bearing clefts surrounded by metalloporphyrins would selectively catch the carbon materials with a curved surface depending on the size of the clefts, which could be adjusted by changing the *syn*-oriented dialkanoacene spacers. The present investigation deals with the recognition ability of designed *syn*-oriented bisporphyrin molecules towards fullerenes C_{60} and C_{70} as the typical carbon materials with a curved surface.

RESULTS AND DISCUSSIONS

Synthesis of diethanoacene-connected bisporphyrins

Since the porphyrin synthesis using 4,7-dihydro-4,7-methanoisoindole suffered low yield [8], we decided to prepare *syn*-oriented bisporphyrins connected with diethanoacenes *syn*-**1** and *syn*-**2** (Fig. 1). *Syn*-oriented bisporphyrin *syn*-**1** was prepared according to a previously reported procedure [9]. Synthesis of *syn*-oriented diethanonaphthacene-bridged bisporphyrin *syn*-**2** was also accomplished according to the similar route as *syn*-**1** (Scheme 1).

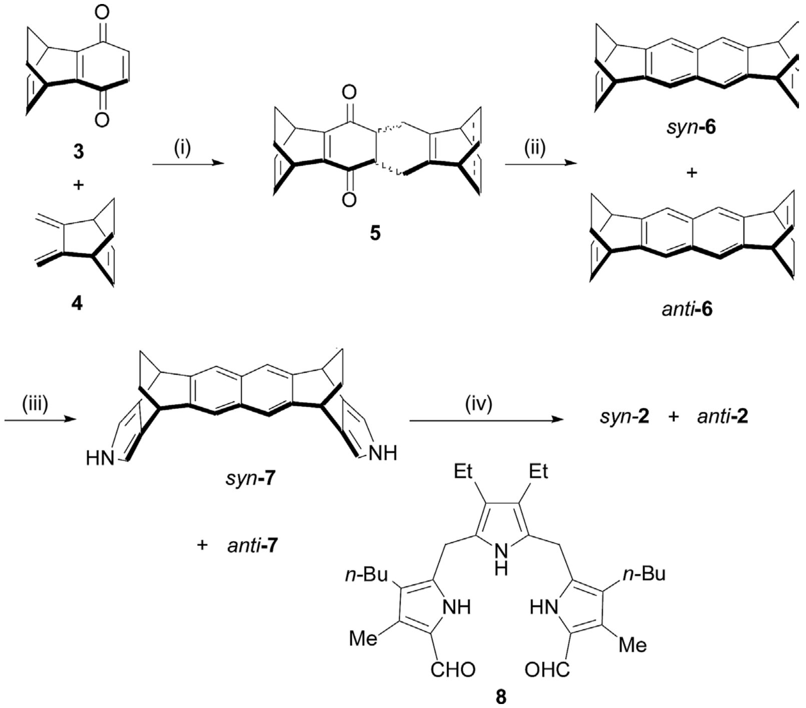


syn-**1**

syn-**2**

Fig. 1. *syn*-oriented bisporphyrins connected with diethanoacenes

The Diels-Alder reaction of ethanoanthraquinone **3** [10] and triene **4** [11] produced naphthacene derivative **5** as a mixture of four isomers in a 69% yield. We failed to determine the diastereomeric ratio. Although one of the desired *syn* isomers was separated by preparative gel-permeation chromatography (GPC) and the structure was unambiguously determined by X-ray analysis, the whole mixture was subjected to the next reaction. Reduction of **5** with $NaBH_4$ and $CeCl_3$ in a 1,4-dioxane/methanol mixture followed by dehydration of the resulted diol with acid produced α,β- and β,γ-unsaturated ketones. Reduction of the ketones with DIBAL followed by dehydration with 4-M hydrochloric acid and successive dehydrogenation with DDQ gave a 1:1 mixture of diethanonaphthacene **6** in a 42% yield (five steps). Although more polar *syn*-**6** was separated from less polar *anti*-**6** by column chromatographic technique on $AgNO_3$-treated silica gel which was effective for the separation of isomeric olefins [12], the 1:1 mixture was employed for the next step. Two pyrrole rings were next constructed at the edged double bonds of **6** by sequential treatment with PhSCl, mCPBA, DBU, a potassium anion of ethyl isocyanoacetate, and KOH in ethylene glycol. A *syn* and *anti* mixture of dipyrrole **7** (1:1 ratio) was obtained in a 47% yield in these five steps. The double [3+1] porphyrin synthesis of dipyrrole **7** with tripyrranedicarbaldehyde **8** [13] provided a 1:1 mixture of targeted *syn*-**2** and *anti*-**2** in a 25% yield. However, we failed to separate the isomers either



Scheme 1. *Reagents, conditions and yields*: (i) $CHCl_3$, 40 °C, 72 h; 69%; (ii) $NaBH_4$, $CeCl_3{\cdot}7H_2O$, 1,4-dioxane/MeOH, 0 °C, 15 min; HCl, THF, 100 °C, 1 h; DIBAL, CH_2Cl_2, -50 °C, 1 h; HCl, CH_2Cl_2, rt, 1 h; DDQ, 1,4-dioxane, rt, 30 min; 42% (five steps); (iii) PhSCl, $CHCl_3$, 0 °C -rt; mCPBA, $CHCl_3$, 0 °C -rt; DBU, CH_2Cl_2, rt; $CNCH_2CO_2Et$, *t*-BuOK, THF, 0 °C -rt; KOH, $(CH_2OH)_2$, 180 °C; 47%; (five steps); (iv) **7**, TFA, CH_2Cl_2, 50 °C, 1 h; Et_3N, chloranil, 0 °C; $Zn(OAc)_2$, $CHCl_3$, rt, overnight; 25%

by chromatography or by recrystallization from chloroform, dichloromethane, and ethyl acetate. Fortunately, recrystallization of the mixture from solvents containing THF afforded red rhombohedral crystals of *syn*-**2**, selectively, which was proven to be suitable for X-ray analysis (*vide post*). A similar result was obtained in the selective preparation of *syn*-**2** by using the separated *syn*-isomer of 1,4,7,10-tetrahydrohydro-1,4;7,10-diethanonaphthacene (*syn*-**6**).

Binding experiments of *syn*-oriented bisporphyrins with fullerenes

The ground state absorption spectrum of *syn*-**2** shows quite similar spectrum of *syn*-**1** [9] and displays a very intense Soret absorption band (λ_{max} = 403 nm), and two Q-bands at 530 and 570 nm. In this case, too, noticeable splitting of the Soret absorption band was not observed, although *syn*-**2** contains two porphyrin chromophores. It was observed that gradual addition of a C_{60} solution to a toluene solution of *syn*-**2** decreases the absorbance of Soret band and red shifted it from 403 to 406 nm. No additional absorption peak was observed in the visible region. An isosbestic point is located at 414 nm, providing very good support in favor of 1:1 complexation between these two species [14]. The stoichiometry of the C_{60}/*syn*-**2** complex was also confirmed by Job's plot. Similar sort of absorption spectral phenomenon was also observed in the case of C_{70}/*syn*-**2** system, though the Soret absorption band has been red shifted by 6 nm probably due to greater interaction between C_{70} and *syn*-**2** compared to C_{60}. An isosbestic point at 412 nm and Job's plot support 1:1 stoichiometry for C_{70}/*syn*-**2** system, too. As the Soret absorption band gets affected more than the Q-absorption bands [15], the gradual decrease in the absorbance of the Soret band of *syn*-**2** was used to determine the binding constant (*K*) for the fullerene/*syn*-**2** complexes. Although we had used Benesi-Hildebrand plot [16] for calculation of binding constants, this method has not been proven to be suitable due to the large *K* values [17]. Thus, titration of *syn*-oriented diethanoanthracene- connected bisporphyrins *syn*-**1** and *syn*-**2** with fullerenes was carried out again and the *K* values of the non-covalent complexes were calculated by applying the non-linear curve-fitting method to changes in absorbance upon the titration [18].

The binding constant *K* values of C_{60}/*syn*-**1** and C_{60}/*syn*-**2** complexes were calculated to be 3.1(4) and 2.1(4) × 10^4 M^{-1}, respectively. The values are fairly large compared to those of the reported thiacalixarene bisporphyrin (*K* = 2340 M^{-1}) [19], terphenyl porphyrin tetramer (*K* = 5800 M^{-1}) [20], and "jaws porphyrin" (*K* = 1950 M^{-1}) [21]; although they are small compared to those of cyclic porphyrin dimers (*K* = 1.1 × 10^5 M^{-1}) [22] and porphyrin hexamer (*K* = 1.4 × 10^8 M^{-1}) [23].

The larger *K* values for C_{70} compared to C_{60} with porphyrins were observed: The *K* values of C_{70}/*syn*-**1** and C_{70}/*syn*-**2** are 5.0(2) × 10^5 and 1.70(13) × 10^5 M^{-1}, respectively. The preference of C_{70} over C_{60} has been commonly observed in the cases of porphyrin hosts [24]. In our case, the values of K_{C70}/K_{C60} of *syn*-**1** and *syn*-**2** were estimated to be 16 and 8 in toluene. Although these values are lower than those of cyclic bisporphyrins (~25 to 32) [22, 25], they are higher than that of calixarene bisporphyrin (~4.3) [19]. The most interesting features of the present investigation are that the K_{C70}/K_{C60} ratio of *syn*-**1** (having narrower cleft) is larger than that of *syn*-**2** and the *K* values of *syn*-**1** with C_{60} and C_{70} are larger than those of *syn*-**2**.

X-ray analysis of *syn*-oriented bisporphyrins with fullerenes

In order to gain insight on the genesis of the complexation of *syn*-**1** and *syn*-**2** towards C_{60} and C_{70}, we carried out explicit X-ray crystallographic analysis. Before

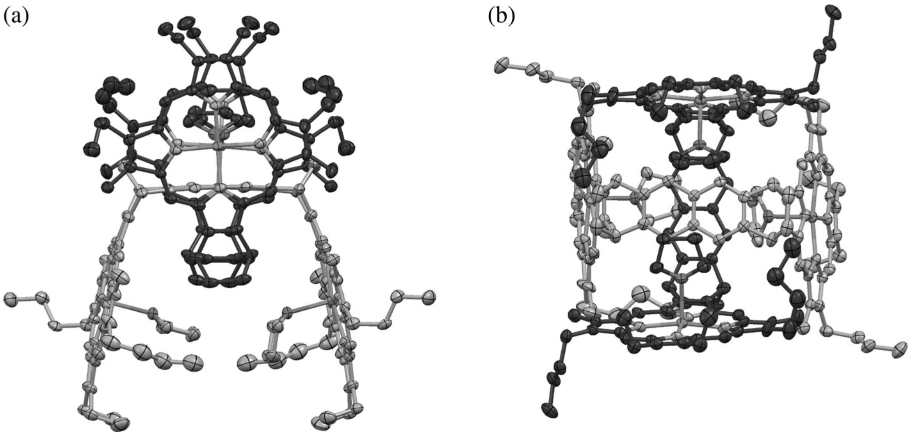


Fig. 2. Side (a) and top (b) Ortep views of pseudo-catenane structure of *syn*-**2** in the crystal. Disordered and hydrogen atoms are omitted for clarity

discussing on the complexes of *syn*-oriented bisporphyrins, namely, *syn*-**1** and *syn*-**2**, the crystal structures without fullerenes should be mentioned. As reported previously [9], *syn*-**1** is crystallized from the mixture of ternary solvent systems containing methanol to form a hexagonal-pillar trimer in which one porphyrin ring of the first molecule stacks inside to one porphyrin ring of the second molecule and remains outside to one porphyrin ring of the third molecule. The intramolecular dihedral angles of the porphyrin mean planes are observed to be *ca.* 60° and almost no strain is observed in these molecules. On the other hand, the crystal structure of *syn*-**2** obtained from solvents containing THF looked interesting and at the same time, was quite different from that of *syn*-**1** (Fig. 2). The porphyrin rings are compressed inwards probably due to the crystal packing. The mean plane angles and Zn–Zn distances of *syn*-**1** and *syn*-**2** are listed in Table 1.

The space group is determined to be I–4. It was observed that in an asymmetric unit, the crystal consists of a half molecule of *syn*-**2**, two molecules of THF, and a quarter molecule of methanol. One of the THF molecules is coordinated to the porphyrin zinc atom of the porphyrin from the concave face in a disordered fashion. One special two-fold rotation axis perpendicularly passes through the center of naphthalene moiety and one of the four special positions (-4) is situated near the concave face of the naphthalene moiety. Therefore, two molecules of *syn*-**2** bearing coordinated THF form a dimeric pseudo-catenane motif. This is the reason behind the selective crystal formation of *syn*-**2**, even from the 1:1 mixture of *syn*-**2** and *anti*-**2**, in the presence of THF. Next, we prepared the 1:1 complexes of bisporphyrins *syn*-**1** and *syn*-**2** with fullerenes for X-ray and NMR analyses. The Ortep drawings are illustrated in Fig. 3 and data concerning the shape of diporphyrins and the relationship between diporphyrins and fullerenes are tabulated in Tables 1 and 2, respectively.

Table 1. Mean plane angles and intramolecular Zn–Zn distances of *syn*-**1** and *syn*-**2**

Crystal		Mean plane angles		Distance, Å
		Porphyrins	Pyrroles[a]	Zn–Zn
Syn-**1**[b,c]	**M-1**	60.94(4)°	63.4(2)°	10.7754(8)
	M-2	59.88(4)°	62.8(2)°	10.8958(7)
	M-3	61.22(4)°	60.7(2)°	10.5202(8)
C60/*syn*-**1**	**C-1**	55.47(4)°	67.4(2)°	11.5010(9)
	C-2	54.08(4)°	71.2(3)°	11.697(1)
C70/*syn*-**1**		57.33(3)°	70.1(2)°	11.6831(5)
Syn-**2**		24.82(2)°	40.0(1)°	10.8110(4)
C60/*syn*-**2**		31.42(2)°	53.3(1)°	12.6518(4)
C70/*syn*-**2**		39.43(2)°	56.1(1)°	12.9759(3)

[a] Junction pyrroles fused to the acene bridges. [b] [9]. [c] Three independent molecules are found. [d] Two independent complexes are found.

In the crystal structure of C_{60}/*syn*-**1**, the main structure was refined without five solvent molecules of heavily disordered THF by the Platon Squeeze technique [26]. Two crystallographically independent complexes were found in an asymmetric unit. Both the C_{60} molecules disorder heavily. The structure is modeled as three disordered C_{60} molecules and the occupancies are calculated to be 0.637, 0.205 and 0.158 in a complex **C-1** (Figs 3a and 3b) and 0.621, 0.214, and 0.165 in another complex **C-2** (Figs 3c and 3d). Both complexes adopt similar structures except for orientation of one methoxy group: methoxy groups orient to the different directions in **C-1**, while both the methoxy groups orient to the endo direction in another complex **C-2**. In both complexes, only one zinc atom is coordinated by THF. Dihedral angles of the mean planes of porphyrin 24 atoms are determined to be 55.47(4)° in **C-1** and 54.08(4)° in **C-2**, although plane dihedral angles of diethanoanthracene-fused pyrrole moieties (junction pyrroles) were estimated to be 67.4(2)° in **C-1** and 71.2(3)° in **C-2** (Table 2). All four porphyrin rings adopt domed out-of-plane distortion and the maximum deviations of β-carbon from the mean planes are estimated to be 0.222(5) (ring Zn1) and 0.254(7) (ring Zn2) Å in the

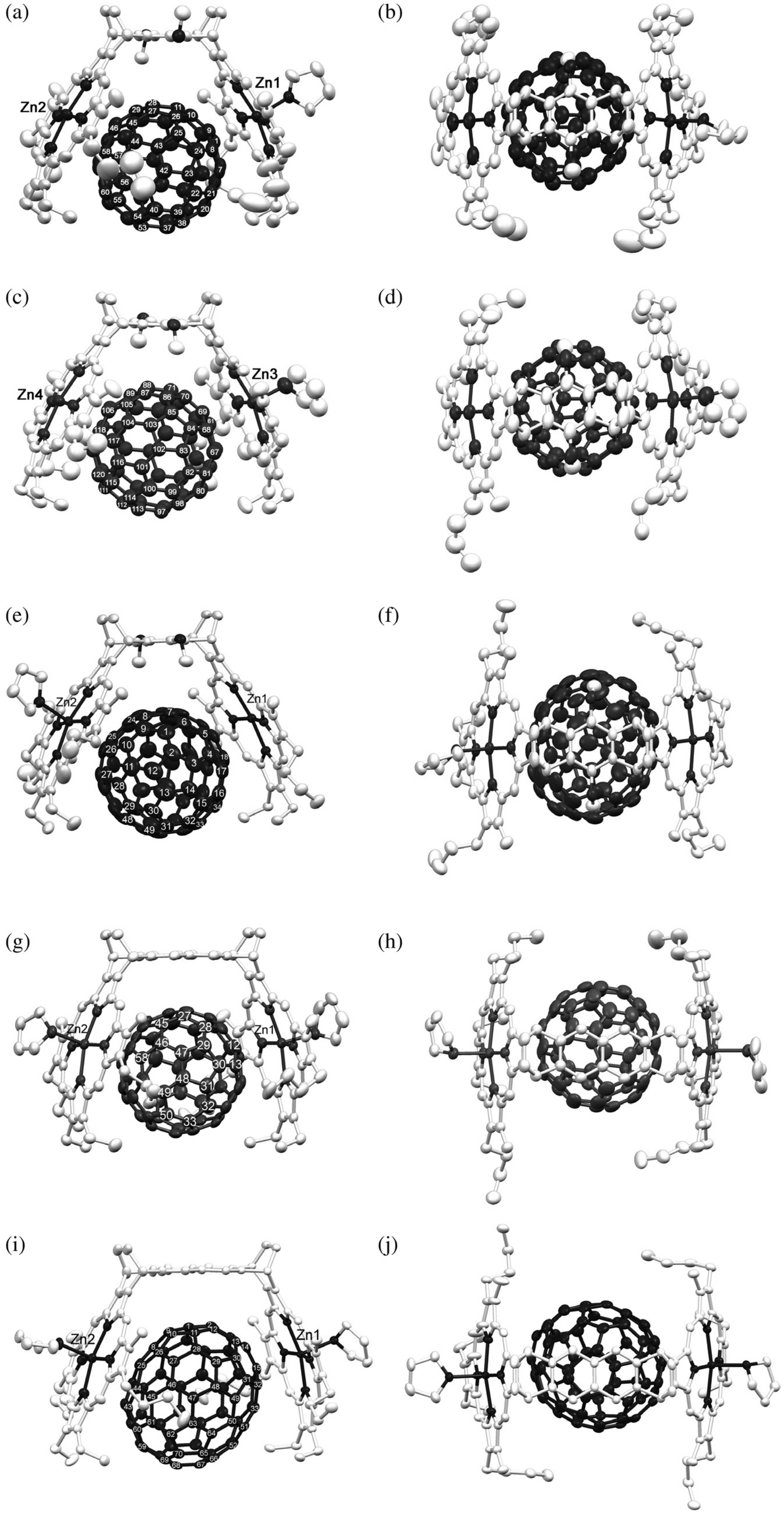


Fig. 3. Ortep drawings of complexes of *syn*-oriented bisporphyrins *syn*-**1** and *syn*-**2** with C_{60} and C_{70}. Side views of a complex (**C1**) of C_{60}/*syn*-**1** (a), another complex (**C2**) of C_{60}/*syn*-**1** (c), C_{70}/*syn*-**1** (e), C_{60}/*syn*-**2** (g), and C_{70}/*syn*-**2** (i); and top views of a complex of C_{60}/*syn*-**1** (b), another complex of C_{60}/*syn*-**1** (d), C_{70}/*syn*-**1** (f), C_{60}/*syn*-**2** (h), and C_{70}/*syn*-**2** (j). Non-coordinated solvent molecules, disordered atoms with minor occupancy, and hydrogen atoms are omitted for clarity

Table 2. Short contact between mean planes of porphyrin rings and fullerene atoms

Crystal		Zn1 porphyrin		Zn2 porphyrin		Acene	
		Position[a], Å		Position[a], Å		Position[a], Å	
C_{60}/*syn*-**1**	**C-1**[b]	C1	2.60(1)	C46	2.65(1)	C28	4.00(1)
		C2	2.73(1)	C58	2.72(1)	C11	4.12(1)
		C501	2.68(2)	C546	2.60(3)	C511	3.97(3)
		C506	2.68(2)	C547	2.68(2)	C528	4.12(2)
		C806	2.58(4)	C846	2.74(4)	C810	4.00(4)
		C801	2.85(3)	C845	2.77(4)	C826	4.25(4)
	C-2[b]	C61	2.59(1)	C106	2.55(1)	C88	3.74(1)
		C62	2.79(1)	C118	2.57(1)	C87	3.93(1)
		C565	2.52(4)	C587	2.57(4)	C569	3.72(2)
		C564	2.81(4)	C605	2.77(3)	C570	3.94(3)
		C862	2.60(4)	C906	2.58(4)	C888	3.85(4)
		C863	2.64(4)	C918	2.75(2)	C871	3.93(4)
C_{70}/*syn*-**1**		C38	2.666(8)	C26	2.701(9)	C22[c]	4.069(9)
		C37	2.713(5)	C25	2.764(9)	C7[c]	4.118(8)
C_{60}/*syn*-**2**		C1	2.645(5)	C57	2.611(5)	C26	3.166(5)
		C2	2.726(5)	C56	2.752(5)	C25	3.313(5)
C_{70}/*syn*-**2**[d]		C15	2.721(1)	C25	2.824(7)	C2	3.255(8)
		C16	2.782(2)	C44	2.847(8)	C12	3.332(1)
		C4A	2.64(1)	C45A	2.74(1)	C11A	3.38(1)
		C3A	2.80(1)	C44A	2.99(1)	C10A	3.42(1)
		C17B	2.73(2)	C46B	2.93(2)	C13B	3.21(2)
		C16B	2.83(4)	C45B	2.99(2)	C12B	3.221(2)

[a] Carbon numbering in the major structure is shown in Fig. 3. [b] Disordered C_{60} atoms with the second and third occupancies are C501–C620 and C801–C920, respectively. [c] There is no bond between these atoms. [d] Disordered atoms with the second and third occupancies are expressed by A and B, respectively.

edge pyrrole rings (opposite to the junction pyrroles) of **C-1**. On the other hand, those are estimated to be 0.187(7) (ring Zn3) and 0.236(6) (ring Zn4) Å in the junction and side pyrrole rings of **C2**, respectively. These observations indicate that the cleft of *syn*-**1** is induced very much to incorporate C_{60} within its cleft by widening the deep part at the bicyclo[2.2.2]octadiene moieties and doming the porphyrin rings to maximize the interaction with the surface of C_{60}. The domed out-of-plane distortion at the porphyrin rings with no coordinated THF is more severe than those with coordinated THF. As there are inversion centers near zinc atoms bearing no coordinated THF, the core porphyrin nitrogen (edge pyrrole) and zinc atoms coordinate to each other of the neighboring molecules. The intermolecular Zn–N distances are 2.667(5) and 2.533(5) Å in **C-1** and **C-2**, respectively. The C_{60} molecule is kept in the deeper part of the *syn*-**1** cleft in the complex **C-2** than in **C-1**, because the closest contact values between the benzene ring and three disordered C_{60} molecules are all shorter in **C-2** (3.72(2)–3.85(4) Å) than in **C-1** (3.97(3)–4.00(4) Å; Table 2). These close contact values are larger than the usual π–π stacking distance (3.4–3.6 Å) [27]. This is also supported by the fact that the dihedral angle of porphyrin rings in **C-1** is wider than in **C-2**, while that of junction pyrroles in **C-1** is narrower than that in **C-2** (Table 1).

The complex of C_{70}/*syn*-**1** was refined by the Platon Squeeze technique. Only one zinc atom is coordinated by THF. The long axis of C_{70} is situated perpendicularly to the molecular axis of *syn*-**1** and therefore, the equatorial part of C_{70} stacks inside to both porphyrin rings (Figs 3e and 3f). The dihedral angle of porphyrin mean planes is calculated to be 57.33(3)°, although the dihedral angle of junction pyrrole moieties is determined to be 70.1(2)°. Both the porphyrin rings adopt domed out-of-plane distortion and the maximum deviations of β-carbon atoms from the mean planes are estimated to be 0.203(4) and 0.268(5) Å in the edge pyrrole rings. As there is an inversion center near the zinc atom without coordinated THF, the core porphyrin nitrogen (edge pyrrole) and the zinc atoms coordinate to each other of the neighboring molecules. The intermolecular Zn–N distances were calculated as 2.650(3) Å. This value is intermediate between those observed in the complexes **C-1** and **C-2** of C_{60}/*syn*-**1**. These observations also indicate deformation of the *syn*-**1** cleft fitting with C_{70} by widening the deep part at the bicyclo[2.2.2]octadiene moieties and doming the porphyrin rings to maximize the interaction with the C_{70} surface. It is interesting to note that the position of C_{70} in the cleft of *syn*-**1** is also intermediate between the complexes of C_{60}/*syn*-**1**, **C-1** and **C-2** (Table 2). The closest contact between C_{70} and the naphthalene moiety is 4.069(9) Å, values of which are out of a common π–π stacking range of 3.4–3.6 Å [26]. Thus, the cleft of *syn*-**1** is also proven to be small for C_{70}.

A very good crystal of C_{60}/*syn*-**2** was obtained and all of the contents in the crystal was found and refined. Both zinc atoms are coordinated by THF molecules, one of which shows disorder, and there are four non-coordinated disordered THF molecules in the asymmetric cell of C_{60}/*syn*-**2** crystal. Both the porphyrin rings adopt domed out-of-plane distortion in order to wrap C_{60} and the maximum deviations of β-carbon atoms from the mean planes were determined to be 0.274(4) and 0.253(3) Å in the junction pyrrole rings (Figs 3g and 3h). It is worthy to note that the dihedral angle of porphyrin mean planes became 31.42(2)°, and, moreover, the dihedral angle of junction pyrrole rings was also reduced to be 53.3(1)°. These facts imply that the cleft of *syn*-**2** is rather large for C_{60}.

In the crystal structure of C_{70}/*syn*-**2** system, the main structure with one dichlorobenzene molecule was refined by the Platon Squeeze technique. Two THF molecules were coordinated to both the zinc atoms. The long axis of C_{70} is situated almost in plane to the molecular axis of *syn*-**2**, the equatorial part of C_{70} stacks inside to one porphyrin ring, and the head part of C_{70} is pointed towards the bicyclo[2.2.2]octadiene junction to another porphyrin ring (Figs 3i and 3j). The dihedral angle of porphyrin mean planes is 39.43(2)° and that of junction pyrrole moieties is 56.1(1)°. These values are only slightly larger than those of C_{60}/*syn*-**2** complex. This also indicates that the cleft of *syn*-**2** is still larger for C_{70} even though the C_{70} molecule lies along the molecular axis of *syn*-**2**. Although both the porphyrin rings adopt domed out-of-plane distortion, the deviation is quite different. The maximum deviation of a β-carbon atom from the mean plane in Zn1 porphyrin ring (right ring in Figs 3e and 3f) is 0.347(3) Å at the edge pyrrole ring, and that in Zn2 porphyrin ring (left ring), to which the equatorial part of C_{70} stacks, is 0.213(9) Å at the edge pyrrole ring. The C_{70} molecule disorders and the occupancies are calculated as 0.490, 0.303 and 0.207. Axes of the second and third disordered C_{70} molecules are tilted by 9.9° and 10.1°, and rotated by 21.2° and 5.9° from the first one, respectively. From Table 2, the close contact distances of fullerenes with the Zn1 porphyrin ring of C_{70}/*syn*-**2** and with both rings of C_{60}/*syn*-**2** are estimated to be in the range between 2.64(1) and 2.83(4) Å, while the distances with the Zn2 porphyrin ring are longer (2.74(1)–2.99(2) Å). This observation is well-rationalized by the lighter domed distortion observed in the Zn2 porphyrin ring of C_{70}/*syn*-**2**.

Due to the domed out-of-plane distortion, distances between the porphyrin mean planes and the closest fullerene carbons are found to be very short in all the crystal structures. No obvious contact either between porphyrin rings or between fullerene molecules was observed in the crystals of *syn*-**2** probably due to coordination of solvent THF and complete incorporation of the fullerene molecules in the cavity of *syn*-**2**. On the other hand, the one-side porphyrin rings of C_{60}/*syn*-**1** and C_{70}/*syn*-**1** stack to themselves of the neighboring molecules. This is probably due to the heavy domed out-of-plane distortion induced by fullerene inclusion to the narrow cleft of *syn*-**1**.

NMR experiments

NMR spectra of *syn*-**1** and *syn*-**2** with or without fullerenes were measured in THF-d_8. The complexes of *syn*-**1** and *syn*-**2** with C_{70} were used for this experiment as C_{70} itself does not dissolve in THF at all and the binding constants of C_{70} with bisporphyrins are larger than those of C_{60}. ^{1}H and ^{13}C NMR spectra are shown in Figs 4 and 5, respectively. All the signals in ^{1}H NMR spectra are unambiguously assigned by ROESY. In both bisporphyrins, obvious up-field shifts were observed after complexation with C_{70}. Signals due to bridge head, inner *meso*,

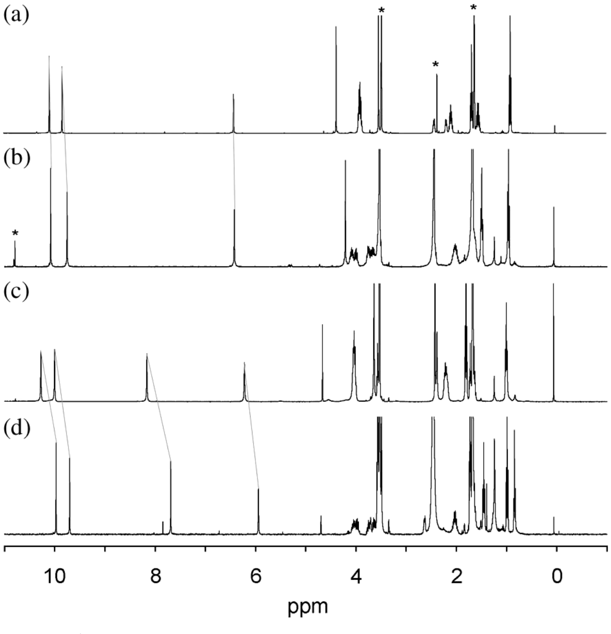


Fig. 4. ^{1}H NMR spectra of (a) *syn*-**1**, (b) C_{70}/*syn*-**1**, (c) *syn*-**2**, and (d) C_{70}/*syn*-**2** in THF-d_8. The signal assignments of *syn*-**1** in spectra (a) and (b) are inner *meso*, outer *meso*, bridge head, and methoxy protons from the lower magnetic field (left). Similarly, four lower signal assignments of *syn*-**2** in spectra (c) and (d) are inner *meso*, outer *meso*, naphthalene, and bridge head protons. Asterisks denote solvent and impurity peaks

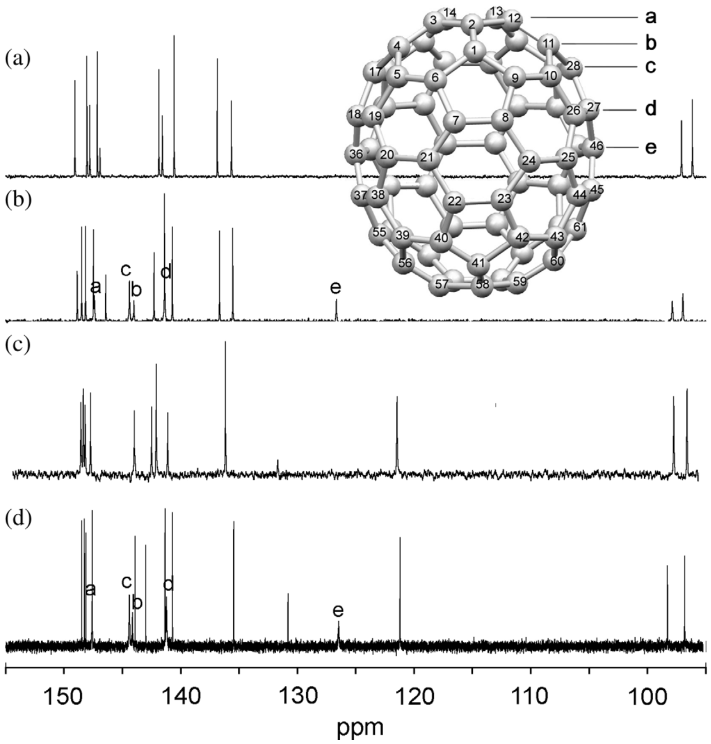


Fig. 5. ^{13}C NMR spectra of (a) *syn*-**1**, (b) C_{70}/*syn*-**1**, (c) *syn*-**2**, and (d) C_{70}/*syn*-**2** in THF-d_8

and outer *meso* protons of bisporphyrin *syn*-**1** exhibit up-field shifts of 0.05, 0.07, and 0.14 ppm. On the other hand, naphthalene, inner *meso*, and outer *meso* protons of complexed *syn*-**2** appear at upper fields of 0.48, 0.31, and 0.31 ppm, respectively. This suggests that the C_{70} moiety stays at the shallow part of the cleft of *syn*-**1**, whereas it is located deep into the cleft of *syn*-**2**.

In ^{13}C NMR (Fig. 5), almost all of the signals due to the presence of the both bisporphyrins and C_{70} show up-field shifts after complexation. As carbon chemical shifts are usually sensitive to conformation, the up-field shifts in bisporphyrins are rather difficult to determine due to the factors: deformation effect of the bisporphyrin by induced fit or diamagnetic ring current effect of C_{70}. On the other hand, the C_{70} molecule is supposed to be rigid enough to discuss the chemical shift by the anisotropic effects of aromatic rings. The up-field shift values of C_{70} chemical shifts compared to the reference chemical shifts in toluene-d_8 [28] are summarized in Table 3. It must be mentioned at this point that the reference chemical shifts of the C_{70} molecule already include the anisotropic effect of solvent toluene-d_8. Therefore, we may neglect the anisotropic effects from the small aromatic moieties such as dimethoxybenzene and naphthalene in the bridging parts.

In both the complexes, signals due to the equatorial carbons of C_{70} show a larger up-field shift. More interestingly, difference of the up-field shifts is larger in the complex of C_{70}/*syn*-**2** than C_{70}/*syn*-**1**. The up-field shifts of the carbons masked **a** and **e** in C_{70}/*syn*-**2** system are estimated to be 3.1 and 4.3 ppm, respectively, whereas those in the case of C_{70}/*syn*-**1** are 3.3 and 4.1 ppm, respectively. This fact presumably suggests that the central part of the C_{70} molecule is more likely to occupy the maximum-shielding position above both the porphyrin rings of *syn*-**2** in the larger cleft. The similar position in *syn*-**1** is not easily accessible for the center part of C_{70}, because the cleft of *syn*-**1** is narrow for C_{70} and the bicycle[2.2.2]octadiene junctions must be widened in order to accept the center part of C_{70} at this position of *syn*-**1**.

Table 3. Up-field shift of C_{70} by complexation with bisporphyrins

Complex	Up-field shift values of C_{70}, ppm[a]				
	a	**b**	**c**	**d**	**e**
C_{70}/*syn*-**1**	3.3	3.4	3.7	4.0	4.1
C_{70}/*syn*-**2**	3.1	3.3	3.7	4.2	4.3

[a] The values were calculated by using those of C_{70} in toluene: **a**, 150.7; **b**, 147.4; **c**, 148.1; **d**, 145.4; and **e**, 130.8 ppm. The carbon assignment of C_{70} is shown in Fig. 5.

EXPERIMENTAL

General

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400, JEOL EX-400, or Bruker AVANCE 500 spectrometer at the ambient temperature. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. EI and FAB spectra were measured with a JEOL JMS-700. The MALDI-TOF MS spectrum was measured with a Voyager DE Pro instrument. Elemental analyzes were performed with a Yanaco MT-5 elemental analyzer. All solvents and chemicals for synthesis were reagent grade quality, obtained commercially, and used without further purification except as noted. Dry dichloromethane and THF were purchased from Kanto Chemical Co. Toluene, triethylamine, and pyridine were distilled from calcium hydride and then stored on Molecular Sieves 4A. Solvents for chromatography were purified by distillation. Thin-layer (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

1,4,5,5a,6,7,10,11,11a,12-decahydro-1,4;7,10-diethanonaphthacene-5,12-dione (5). A solution of 5,6-dimethylenebicyclo[2.2.2]oct-2-ene (**4**; 1.27 g, 9.61 mmol) and 5,8-dihydro-5,8-ethano-1,4-naphthoquinone (**3**; 0.62 g, 3.32 mmol) in $CHCl_3$ (25 mL) was heated at

40 °C for three days under N_2. After cooling, the solvent was removed and the residue was chromatographed on silica gel (80% $CHCl_3$/hexane). Fractions of R_f: 0.35–0.47 were collected and concentrated to afford 0.73 g (69%) of the title compound as a mixture of four possible diastereomers: a pale yellow solid, mp 152–155 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.15–1.50 (8H, m), 2.15–2.28 (2H, m), 2.32–2.50 (2H, m), 3.05–3.18 (2H, m), 3.20–3.30 (2H, br m), 4.24 (2H, br s), 6.22–6.28 (2H, m), 6.30–6.39 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ, ppm 24.42, 24.44, 25.20, 25.52, 26.46, 26.51, 34.22, 34.27, 41.07, 41.24, 47.61, 47.72, 47.85, 48.03, 133.56, 133.60, 133.92, 134.06, 151.11, 151.17, 196.16, 196.34. IR (KBr): ν_{max}, cm^{-1} 1670, 1269, 688. MS (EI, rel. intensity): *m/z* 318 ($[M]^+$, 100), 290 (23) 262 (55) 244 (50) 234 (31). HRMS (EI): *m/z* calcd. for $C_{22}H_{22}O_2$: 318.1620. Found: Mr, 318.1620. One of the isomers could be separated by preparative GPC; ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.24 (4H m), 1.30 (2H, m), 1.44 (2H, m), 2.20 (2H, dd, *J* = 14.9, 4.4 Hz), 2.46 (2H, dd, *J* = 14.9, 4.4 Hz), 3.09 (2H, t, *J* = 4.4 Hz), 3.24 (2H, br s), 4.24 (2H, br s), 6.22 (2H, m), 6.33 (2H, m). Stereochemistry of this isomer was unambiguously determined as a *syn,syn*-isomer by X-ray analysis.

***Syn*- and *anti*-1,4,7,10-tetrahydro-1,4;7,10-diethanonaphthacene (*syn*-6 and *anti*-6).** To a solution of naphthacenedione **5** (0.65 g, 2.04 mmol) and $CeCl_3{\cdot}7H_2O$ (1.52 g, 4.07 mmol) in a mixture of dry methanol (3.8 mL) and dry dioxane (80 mL) was added $NaBH_4$ (0.16 g, 4.0 mmol) at 0 °C under N_2 and the mixture was stirred at rt for 15 min. The reaction was quenched with water and the mixture filtrated through a Celite pad. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to afford 0.66 g (100%) of 1,4,5,5a,6,7,10,11,11a,12-decahydro-1,4;7,10-diethanonaphthacene-5,12-diol as a mixture of diastereomers: a white solid, mp 110–126 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$, typical signal): δ, ppm 6.24–6.38 (4H, m). There were many signals between 1.0 and 5.5 ppm with various integral ratios. ^{13}C NMR (100 MHz, $CDCl_3$; typical signals): δ, ppm 24.44, 24.54, 24.76, 24.84, 24.95, 25.04, 25.30, 25.40, 25.48, 25.56, 25.84, 26.07, 31.49, 33.06, 33.08, 33.28, 33.31, 34.59, 36.12, 37.38, 40.98, 41.02, 41.29, 41.38, 41.49, 41.55, 44.89, 45.37, 45.44, 66.99, 69.22, 70.06, 70.14, 70.35, 70.88, 70.90, 131.99, 132.19, 133.06, 133.24, 134.02, 134.13, 134.17, 134.25, 134.30, 134.59, 134.68, 134.76, 134.97, 135.09, 135.22, 135.37, 135.56, 135.59, 135.69, 138.36, 138.40, 139.04. IR (KBr): ν_{max}, cm^{-1} 3435, 1653, 687. MS (EI, rel. intensity): *m/z* 322 ($[M]^+$, 6), 304 (32), 302 (75), 274 (58), 246 (100). HRMS (EI): *m/z* calcd. for $C_{22}H_{26}O_2$: 322.1933. Found: Mr, 322.1937. This material was used in the next step without purification.

To a solution of the diol (5.67 g, 17.6 mmol) in $CHCl_3$ (180 mL) was added 4-M HCl (9.8 mL) and the mixture was heated at 100 °C for 1 h under N_2. The mixture was cooled to rt and an aqueous saturated solution of $NaHCO_3$ was added. The mixture was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$, R_f 0.5) and then recrystallized from $CHCl_3$/ether to afford 2.51 g (47%) of 1,4,5,5a,6,7,10,11,11a,12-decahydro-1,4;7,10-diethanonaphthacen-5-one as a diastereomeric mixture: a white solid, mp 143–146 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.20–1.39 (8H, m), 1.88 (1H, m), 2.13 (1H, m), 2.15–2.55 (4H, m), 3.20–3.28 (2H, m), 3.45 (1H, m), 4.19 (1H, m), 6.15–6.37 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ, ppm 24.36, 24.62, 25.10, 25.33, 25.34, 25.41, 25.55, 25.63, 25.64, 25.80, 25.91, 25.96, 31.12, 31.17, 31.45, 32.97, 33.29, 34.00, 40.86, 41.34, 42.81, 42.84, 44.85, 45.18, 45.29, 45.63, 131.72, 131.91, 133.86, 133.94, 134.03, 134.08, 134.21, 134.24, 134.28, 135.28, 135.42, 135.46, 135.55, 135.60, 136.46, 204.99, 206.76. IR (KBr): ν_{max}, cm^{-1} 1654, 1392, 1271, 1147, 688. MS (EI, rel. intensity): *m/z* 304 ($[M]^+$, 25), 276 (31), 248 (100). Anal. calcd. for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.48; H, 7.86%.

To a solution of naphthacenone (0.21 g, 0.69 mmol) in dry CH_2Cl_2 (6.8 mL) was added 1-M DIBAL (1.1 mL, 1.1 mmol) and the mixture was stirred at -50 °C for 1 h. The reaction mixture was warmed up to rt and a 5% aqueous solution of HCl was added. After the mixture was stirred at rt for 1 h, the mixture was neutralized with an aqueous solution of $NaHCO_3$. The mixture was filtrated through a Celite pad. The filtrate was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$, R_f 0.89) and then recrystallized from $CHCl_3$/ether to afford 0.19 g (97%) of 1,4,5,5a,7,10,11a,12-octahydro-1,4;7,10-diethanonaphthacene as a white powder: mp 122–124 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.20–1.36 (4H, m), 1.38 (2H, m), 1.54 (2H, m), 1.84–2.00 (2H, m), 2.00–2.20 (2H, m), 2.25–2.40 (2H, m), 3.11 (2H, br m), 3.18–3.25 (2H, m), 5.20–5.30 (2H, m), 6.15–6.30 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ, ppm 25.66, 25.69, 26.29, 26.46, 26.63, 30.04, 30.07, 30.20, 30.27, 33.39, 33.52, 33.64, 33.76, 35.74, 38.95, 38.92, 41.54, 41.63, 120.12, 120.26, 120.38, 120.59, 132.81, 132.88, 134.23, 134.28, 136.40, 136.68, 136.82, 138.91. IR (KBr): ν_{max}, cm^{-1} 2947, 692. MS (EI, rel. intensity): *m/z* 288 ($[M]^+$, 8), 260 (56), 232 (12), 128 (100). Anal. calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.26; H, 8.43%.

To a solution of octahydrodiethanonaphthacene (0.22 g, 0.78 mmol) in dry dioxane (24 mL) was added DDQ (0.53 g, 2.34 mmol) and the mixture was stirred at rt for 30 min under N_2. The reaction mixture was filtrated and the filtrate was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane, R_f 0.65) and recrystallized from $CHCl_3$/ether to afford 0.20 g (92%) of the title compound as a mixture of two isomers: a white powder: mp > 211 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.49–1.51 (4H of both isomers, m), 1.61–1.63 (4H of both isomers, m), 3.99 (4H of both isomers, br s), 6.52 (4H of *syn* isomer, m), 6.53 (4H of *anti* isomer, m), 7.48 (4H of *anti* isomer, s), 7.49 (4H of *syn* isomer, s). ^{13}C NMR (100 MHz, $CDCl_3$) *syn*-**6**: δ, ppm 26.22, 40.05, 119.86, 130.28, 134.99, 141.85; *anti*-**6**: δ, ppm 26.19, 40.08, 119.88, 130.28, 135.05, 141.86. IR (KBr): ν_{max}, cm^{-1} 2949, 1608, 1485, 1132, 1105, 897, 683. MS (EI, rel. intensity): *m/z* 284 ([M]$^+$, 22), 256 (35), 228 (100). Anal. calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.53; H, 7.12%. The isomers could be separated by column chromatography on $AgNO_3$-treated silica gel (10% EtOAc/hexane, R_f *anti*, 0.25; *syn*, 0.04). The separation of 200 mg of this mixture gave 90 and 97 mg of *syn*- and *anti*-isomers (*syn*-**6** and *anti*-**6**), respectively. In order to dermine the stereochemistry of the isomers, X-ray analysis of the polar isomer was carried out. However, the ethano and etheno parts of **6** completely disordered in the crystal. Therefore, the stereochemistry could not be determined by the X-ray analysis.

Conversion of dihydrodiethanonaphthacene 6 to dipyrrole 7. To a solution of **6** (0.49 g, 1.72 mmol) in dry CH_2Cl_2 (28.9 mL) was added PhSCl (0.41 mL, 3.44 mmol) at 0 °C and the mixture was stirred at rt for 30 min. The reaction mixture was quenched with an aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane, R_f 0.72–0.50) and triturated with ether to afford 1.01 g (100%) of bis-adduct of PhCl as a diastereomer mixture: a white powder; mp 190–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.35–1.50 (2H, m), 1.50–70 (2H, m), 1.95–2.08 (2H, m), 2.40–2.53 (2H, m), 3.23 (2H, m), 3.69 (2H, m), 3.65–3.75 (2H, m), 3.93 (2H, m), 7.22–7.35 (8H, m), 7.40–7.50 (2H, m), 7.60–7.70 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) *syn*-isomers: δ, ppm 18.90, 26.48, 26.62, 40.34, 40.50, 42.99, 57.31, 57.33, 64.94, 65.10, 122.61, 122.67, 123.86, 127.17, 127.20, 128.91, 129.03, 131.90, 131.94, 132.26, 132.31, 132.44, 134.32, 134.39, 136.91, 136.99, 138.10, 138.22; *anti*-isomers: δ, ppm 18.89, 26.42, 40.36, 40.39, 43.00, 43.02, 57.44, 65.05, 122.69, 122.74, 123.99, 124.04, 127.07, 127.24, 127.44, 128.97, 131.96, 132.35, 134.44, 136.92, 137.04, 138.16, 138.28. IR (KBr): ν_{max}, cm^{-1} 1647, 1522, 906, 690. MS (EI, rel. intensity): *m/z* 572 ([M]$^+$, 100), 536 (20), 500 (18), 463 (47), 427 (47). Anal. calcd. for $C_{34}H_{30}Cl_2S_2$: C, 71.19; H, 5.27. Found: C, 71.09; H, 5.23%.

To a solution of the bis-adduct (1.01 g, 1.76 mmol) in CH_2Cl_2 (47 mL) was added mCPBA (2.17 g, 8.80 mmol) at 0 °C and the mixture was stirred at rt for 1 h. The reaction mixture was quenched with an aqueous solution of Na_2SO_3 and $NaHCO_3$. The mixture was filtrated through a Celite pad. The filtrate was extracted with EtOAc. The organic layer was washed successively with an aqueous solution of $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (40% EtOAc/hexane, R_f = 0.53, 0.44) and recrystallized from $CHCl_3$/ether to give 0.91 g (81%) of bis-sulfone as a diastereomer mixture: a white powder, mp > 103 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.30–1.50 (2H, m), 1.50–1.70 (2H, m), 1.98–2.10 (2H, m), 2.30–2.45 (2H, m), 3.37 (2H, m), 3.55–3.70 (2H, m), 3.75–3.90 (2H, m), 4.28–4.40 (2H, m), 7.35–7.80 (14H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) *syn*-isomers: δ, ppm 18.55, 27.16, 27.35, 34.47, 34.88, 42.91, 57.02, 57.16, 73.02, 73.16, 122.50, 122.81 123.74, 123.79, 128.78, 128.82, 129.12, 129.16, 132.60, 134.10, 134.34, 135.46, 135.58, 137.04, 137.56 149.00; *anti*-isomers: δ, ppm 18.63, 27.02, 34.75, 42.99, 56.85, 122.73, 123.93, 128.40, 128.66, 129.17, 132.49, 132.91, 133.86, 135.48, 136.81, 138.32, 148.16. IR (KBr): ν_{max}, cm^{-1} 1319, 1149, 1086, 735, 534. MS (EI, rel. intensity): *m/z* 636 ([M]$^+$, 88), 600 (55), 572 (100), 536 (50), 508 (51. HRMS (EI): *m/z* calcd. for $C_{34}H_{30}Cl_2O_4S_2$, 636.0963. Found: *Mr* 636.0961. Anal. calcd. for $C_{34}H_{30}Cl_2O_4S_2$ + 1/2H_2O: C, 63.15; H, 4.83. Found: C, 64.04; H, 4.74%.

To a solution of bis-sulfone (0.58 g, 1.02 mmol) in dry CH_2Cl_2 (40 mL) was added DBU (0.61 mL, 4.07 mmol) and the mixture was stirred for 1 h. The reaction mixture was neutralized with 1% aqueous HCl and extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (50% EtOAc/hexane, R_f 0.65, 0.53) and then recrystallized from $CHCl_3$/ether to afford 0.48 g (84%) of α,β-unsaturated bis-sulfone as a diastereomeric mixture: a white powder, 133–155 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.57–1.69 (8H, m), 4.24 (2H, m), 4.29 (2H, m), 7.24 (2H, m), 7.30–7.46 (4H, m), 7.49–7.55 (6H, m), 7.80–7.82 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ, ppm 14.17, 21.01, 25.84, 26.45, 26.48, 40.22, 41.11, 60.27, 120.54, 120.61, 120.97, 127.56, 129.00, 130.31, 130.34, 130.46, 130.60, 133.11, 133.15, 138.93, 138.96, 138.99, 139.10, 139.14, 139.37, 139.40, 144.24, 146.82, 146.80, 146.89. IR (KBr): ν_{max}, cm^{-1} 1304, 1151, 1092, 725, 569. MS (EI, rel. intensity): *m/z* 564 ([M]$^+$, 39), 536 (53), 508 (100). HRMS (EI): *m/z* calcd. for $C_{34}H_{28}O_4S_2$: 564.1429. Found: *Mr*, 564.1431. Anal. calcd. for $C_{34}H_{28}O_4S_2$ + 1/2H_2O: C, 71.18; H, 5.09. Found: C, 72.24; H, 4.97%.

To a solution of the α,β-unsaturated bis-sulfone (0.79 g, 1.40 mmol) and ethyl isocyanoacetate (0.37 mL, 3.36 mmol) in dry THF (20 mL) was added 1-M *t*-BuOK (3.92 mL, 3.92 mmol) at 0 °C under N_2. The mixture was stirred at 0 °C for 20 min and then at rt for 2 h. The reaction mixture was quenched with water. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (30% EtOAc/hexane, R_f, 0.20–0.32) and recrystallized from $CHCl_3$/ether to afford 0.59 g (84%) of dipyrroledicarboxylate diester as a mixture of four isomers: a white powder, mp > 276.4 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.20–1.40 (6H, m), 1.7–1.82 (8H, m), 4.30–4.40 (6H, m), 4.86 (2H, br s), 6.67 (2H, m), 7.49–7.54 (2H, m), 7.58–7.61 (2H, m), 8.42 (2H, br s). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ, ppm 14.23, 14.23, 27.64, 28.29, 37.31, 37.72, 59.92, 60.37, 113.73, 114.68, 114.71, 120.38, 120.44, 121.06, 121.12, 130.10, 130.15, 130.59, 130.61, 135.16, 135.24, 141.62, 142.29, 142.34, 161.50. IR (KBr): ν_{max}, cm^{-1} 3313, 2951, 2866, 1683, 1317, 1141. MS (DI-EI, rel. intensity): *m/z* 506 ([M]$^+$, 21), 478 (100), 358 (40). HRMS (DI-EI): *m/z* calcd. for $C_{32}H_{30}N_2O_4$: 506.2206. Found: *Mr*, $C_{32}H_{30}N_2O_4$, 506.2204. Anal. calcd. for $C_{32}H_{30}N_2O_4$ + 1/4$CHCl_3$: C, 72.21; H, 5.68; N, 5.22. Found: C, 71.89; H, 5.85; N 5.08%.

A solution of dipyrroledicarboxylate diester (0.15 g, 0.30 mmol) and KOH (0.59 g) in ethylene glycol (11.5 mL) was heated at 180 °C for 2 h under N_2 in the dark. After being cooled, the reaction mixture was diluted with water. The resulted suspension was filtrated and the white precipitates were washed with water. The filtrate was extracted with EtOAc. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to leave a white solid. The obtained solid materials were combined and dissolved in $CHCl_3$. The solution was passed through a short silica-gel column. The filtrate was concentrated to give 87.8 mg (82%) of dipyrrole **7** as a white powder: mp > 295 °C (docomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.70–1.83 (8H, m), 4.34 (4H, s), 6.56 (4H, d, *J* = 3.8 Hz), 7.51 (4H, s), 7.56 (2H, br s). ^{13}C NMR (100 MHz, $CDCl_3$, signals due to *syn* and *anti* isomers overlapped completely): δ, ppm 28.75, 37.35, 108.65, 120.27, 127.99, 130.53, 142.76. IR (KBr): ν_{max}, cm^{-1} 1522, 1043, 906, 775, 559. MS (EI, rel. intensity): *m/z* 362 ([M]$^+$, 33), 334 (100), 306 (74), 153 (60). HRMS (EI): *m/z* calcd. for $C_{26}H_{22}N_2$: 362.1783. Found: *Mr*, 362.1782. Anal. calcd. for $C_{26}H_{22}N_2$ + 1/4CH_2Cl_2: C, 82.17; H, 5.91; N, 7.30. Found: C, 81.91; H, 6.06; N 7.10%.

[3+1] Porphyrin synthesis. To a solution of dipyrrole **7** (84.4 mg, 0.233 mmol) and tripyrrane **8** (222.5 mg, 0.466 mmol) in dry CH_2Cl_2 (30.2 mL) was added trifluoroacetic acid (0.94 mL, 12.6 mmol) and the mixture was stirred at 50 °C for 1 h under N_2 in dark. The reaction mixture was cooled to 0 °C and neutralized with triethylamine (1.56 mL, 11.2 mmol). Chloranil (115 mg, 0.466 mmol) was added and the mixture was stirred for 1 h. The reaction mixture was quenched with an aqueous solution of $Na_2S_2O_3$ and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with water, an aqueous saturated solution of $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (35 mL) and $Zn(OAc)_2\cdot 2H_2O$ (0.102 g, 0.466 mmol) was added. The mixture was stirred at rt under N_2 overnight. The reaction mixture was washed with water and an aqueous saturated solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$, R_f, 0.88) and recrystallized from THF/MeOH to afford 80.4 mg (25%) of the title compound as a mixture of two isomers: a purple powder. mp > 287 °C (decomp). UV-vis ($CHCl_3$): δ_{max}, nm (log ε) 402 (5.61), 532 (4.42), 569 (4.45). IR (KBr): ν_{max}, cm^{-1} 1697, 1647, 1522, 1458, 457. MS (MALDI-TOF): *m/z* 1369.6252 [M$^+$ + 5], 1342.8574 [M$^+$ + 6 - (C_2H_4)], 1313.6990 [M$^+$ + 5 - 2(C_2H_4)]. HRMS (FAB$^+$): *m/z* calcd. for $C_{86}H_{92}N_8Zn_2$ + H$^+$ - (2C_2H_4): 1309.5482. Found: 1309.5480. *Syn* isomer ***syn*-2** was obtained by recrystallization from THF/MeOH or THF/hexane. ***syn*-2.** ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 1.04 (12H, t, *J* = 7.8 Hz), 1.55–1.67 (8H, m), 1.84 (12H, t, *J* = 7.6 Hz), 2.19–2.23 (8H, m), 2.35 (4H, m), 2.45 (4H, m), 3.67 (12H, s), 4.01–4.05 (16H, m), 6.23 (4H, s), 8.22 (4H, s), 10.04 (4H, s), 10.31 (4H, s). ^{13}C NMR (100 MHz, THF-d_8): δ, ppm 10.52, 10.61, 13.20, 13.29, 16.36, 17.77, 17.86, 19.10, 19.19, 22.40, 22.50, 24.62, 25.01, 25.58, 25.68, 29.27, 35.13, 35.22, 39.73, 39.82, 95.83, 95.93, 96.99, 97.06, 120.69, 130.88, 135.39, 135.49, 140.32, 140.43, 141.32, 141.42, 141.71, 141.80, 143.19, 146.93, 147.04, 147.41, 147.57, 147.68, 147.77, 147.87.

X-ray experiments

Since both the bisporphyrins and fullerenes were readily soluble in chlorinated aromatic hydrocarbons, equivalent molar amounts of these compounds were dissolved in chlorobenzene. Then, the solvent was thoroughly removed *in vacuo* to leave red powderly solids, which were subsequently recrystallized from a THF/MeOH solvent system to obtain the 1:1 complexes. These complexes were dissolved in THF containing no or a small amount of toluene, chlorobenzene, or *o*-dichlorobenzene, and then placed in a vapor of heptane, methanol, or 2-propanol. Single crystals of C_{60}/*syn*-**1** (from THF/PhCl/2-propanol), C_{70}/*syn*-**1** (from THF/PhCl/methanol), C_{60}/*syn*-**2** (from THF/2-propanol), and C_{70}/*syn*-**2** (from THF/*o*-$C_6H_4Cl_2$/heptane) were obtained. The crystal of *syn*-**2** was taken in a Lindeman capillary tube with a very small amount of the mother liquor, and then the capillary tubes were sealed by candle flame. Other crystals were scooped by cryo-loops. Determination of cell parameters and collection of reflection intensities were performed on Rigaku Mercury-8 (Mo, 3-kW sealed tube), VariMax Rapid (Cu, 2-kW rotating anode), or FR-E R-AXIS HR IP instrument (Mo, 1.8-kW rotating anode) at low temperatures. Data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct method (SIR2004[29]) and expanded using the Fourier technique [30]. Hydrogen atoms were placed in calculated positions and refined by using riding models. All calculations were performed by using the CrystalStructure crystallographic software package [31] or WinGX [32]. Shelxl-97 [33] was used for structure refinement.

In the cases of C_{70}/*syn*-**1**, *syn*-**2**, and C_{70}/*syn*-**2**, there were many strong electron peaks near the disordered non-coordinated solvent molecules. We failed to model them properly. Therefore, the original diffraction data were modified by the Platon Squeeze technique [26] in order to refine the structure without the disordered non-coordinated solvent molecules. As significant alerts concerning large positive electron peaks forming hexagon, pentagon, and their fused structures on the fullerene surface were created by Platon CIF check after the refinement without disorder treatment of fullerenes, another fullerene molecule was created and thus fullerenes were treated as disordered in these cases. Carbon atoms in the second fullerene molecule were placed at the electron peaks or at some carbon atoms of the first molecule in order to form a rational shape of fullerenes. Then, the structures and occupancies were refined by restraining all bond distances and angles in the fullerene structures with the reported values [31], as well as all thermal factors. After convergence, the CIF check was performed. This cycle was repeated once more until no significant alert of positive electron peaks in CIF check was created.

Crystal data for *syn,syn*-**5**: $C_{22}H_{22}O_2$ 0.20 × 0.20 × 0.13 mm, *monoclinic*, space group *P2₁/n*, $a = 11.691(3)$, $b = 11.671(2)$, $c = 12.234(3)$ Å, $\beta = 104.075(5)°$, $V = 1619.2(6)$ Å^3, Mo *K*α, $T = 298$ K, $Z = 4$, $\rho_{calcd} = 1.306$ g.cm^{-3}, $\mu = 0.082$ mm^{-1}, *F(000)* = 680. 16716 measured, 3697 unique, 3016 observed [I > 2σ(I)], $R_{merge} = 0.0259$; $R_1 = 0.0545$ [I > 2σ(I)], $wR_2 = 0.1491$ (all); GOF = 1.095. CCDC number 740154. *syn*-**6**: $C_{22}H_{20}$ 0.30 × 0.30 × 0.16 mm, *triclinic*, space group *P–1*, $a = 6.0056(5)$, $b = 6.3096(5)$, $c = 10.0269(11)$ Å, $\alpha = 83.421(7)°$, $\beta = 82.631(7)°$, $\gamma = 81.040(7)°$, $V = 370.47(6)$ Å^3, Mo *K*α, $T = 150$ K, $Z = 1$, $\rho_{calcd} = 1.275$ g.cm^{-3}, $\mu = 0.072$ mm^{-1}, *F(000)* = 152. 4176 measured, 1654 unique, 1469 observed [I > 2σ(I)], $R_{merge} = 0.0127$; $R_1 = 0.0477$ [I > 2σ(I)], $wR_2 = 0.1321$ (all); GOF = 1.061. CCDC number 740155. C_{60}/*syn*-**1**·THF: Squeezed, refined crystal formula: $C_{296}H_{204}N_{16}O_6Zn_4$ 0.30 × 0.10 × 0.10 mm, *triclinic*, space group *P–1*, $a = 14.0926(3)$, $b = 27.7138(5)$, $c = 28.8066(5)$ Å, $\alpha = 84.7500(10)°$, $\beta = 85.3680(10)°$, $\gamma = 87.2440(10)°$, $V = 11157.5(4)$ Å^3, Cu *K*α, $T = 100$ K, $Z = 2$, $\rho_{calcd} = 1.292$ g.cm^{-3}, $\mu = 1.013$ mm^{-1}, *F(000)* = 4520. 209929 measured, 40109 unique, 22883 observed [I > 2σ(I)], $R_{merge} = 0.0359$; $R_1 = 0.0819$ [I > 2σ(I)], $wR_2 = 0.1845$ (all); GOF = 1.041. CCDC number 802620. C_{70}/*syn*-**1**·THF: Squeezed, refined crystal formula: $C_{158}H_{102}N_8O_3Zn_2$ 0.50 × 0.40 × 0.30 mm, *triclinic*, space group *P–1*, $a = 15.742(2)$, $b = 16.3094(16)$, $c = 27.020(3)$ Å, $\alpha = 80.390(4)°$, $\beta = 73.300(5)°$, $\gamma = 68.970(5)°$, $V = 6186.0(13)$ Å^3, Mo *K*α, $T = 133$ K, $Z = 2$, $\rho_{calcd} = 1.230$ g.cm^{-3}, $\mu = 0.448$ mm^{-1}, *F(000)* = 2380. 97566 measured, 27506 unique, 18422 observed [I > 2σ(I)], $R_{merge} = 0.0972$; $R_1 = 0.0834$ [I > 2σ(I)], $wR_2 = 0.2246$ (all); GOF = 1.068. CCDC number 798877. *Syn*-**2**·4THF: Squeezed, refined crystal formula: $C_{102}H_{124}N_8O_4Zn_2$ 0.30 × 0.30 × 0.15 mm, *tetragonal*, space group *I–4*, $a = 21.4611(4)$, $b = 21.4611(4)$, $c = 19.8517(5)$ Å, $V = 9143.3(3)$ Å^3, Mo *K*α, $T = 150$ K, $Z = 4$, $\rho_{calcd} = 1.204$ g.cm^{-3}, $\mu = 0.580$ mm^{-1}, *F(000)* = 3536. 25974 measured, 10426 unique, 9172 observed [I > 2σ(I)], $R_{merge} = 0.0250$; $R_1 = 0.0503$ [I > 2σ(I)], $wR_2 = 0.1437$ (all); GOF = 1.106. CCDC number 740157. C_{60}/*syn*-**2**·6THF: crystal formula: $C_{170}H_{140}N_8O_6Zn_2$ 0.30 × 0.40 × 0.05 mm, *triclinic*, space group *P–1*, $a = 14.7142(3)$, $b = 15.6627(3)$, $c = 29.1528(6)$ Å, $\alpha = 104.6547(7)°$, $\beta = 91.1697(7)°$, $\gamma = 109.9529(8)°$, $V = 6067.7(2)$ Å^3, Cu *K*α, $T = 100$ K, $Z = 2$, $\rho_{calcd} = 1.380$ g.cm^{-3}, $\mu = 1.027$ mm^{-1}, *F(000)* = 2648. 112983 measured, 21850 unique, 15563 observed [I > 2σ(I)], $R_{merge} = 0.0419$; $R_1 = 0.0604$ [I > 2σ(I)], $wR_2 = 0.1722$ (all); GOF = 1.021. CCDC number 798876. C_{70}/*syn*-**2**·*o*-$C_6H_4Cl_2$·2THF: Squeezed, refined crystal formula: $C_{170}H_{112}Cl_2N_8O_2Zn_2$ 0.50 × 0.40 × 0.30 mm, *monoclinic*, space group *P2₁/c*, $a = 33.778(5)$, $b = 14.6329(19)$, $c = 26.871(4)$ Å, $\beta = 106.4820(10)°$, $V = 12736(3)$ Å^3, Mo *K*α, $T = 100$ K, $Z = 4$, $\rho_{calcd} = 1.304$ g.cm^{-3}, $\mu = 0.481$ mm^{-1}, *F(000)* = 5192. 57583 measured, 29007 unique, 21464 observed [I > 2σ(I)], $R_{merge} = 0.0300$; $R_1 = 0.0718$ [I > 2σ(I)], $wR_2 = 0.2201$ (all); GOF = 1.117. CCDC number 740157.

CONCLUSION

We have prepared newly designed *syn*-oriented bisporphyrin, namely, *syn*-**2** (bearing diethanonaphthacene as a spacer) and then, compared with previously reported *syn*-**1**, which contains dimethoxydiethanoanthacene as a spacer unit. Binding experiments suggest that both *syn*-**1** and *syn*-**2** spontaneously form 1:1 complexes with fullerenes C_{60} and C_{70}. The larger value of binding constants were observed in case of *syn*-**1** with both the fullerenes. The selectivity in binding constant, *viz.*, K_{C70}/K_{C60}, is found to be larger for *syn*-**1** (16) than that of *syn*-**2** (8). The selectivity ratio is moderate among those reported so far.

The X-ray analysis shows that the bisporphyrin skeletons are distorted in order to maximize the interaction between bisporphyrins and the fullerenes. The bicyclo[2.2.2]octadiene moieties were widened and get narrower by complexation with the fullerenes in the cases of *syn*-**1** and *syn*-**2**, respectively. This fact means that the cleft of *syn*-**1** is a little smaller for the fullerenes, while that of *syn*-**2** is slightly larger. Therefore, C_{70} occupies a rather shallow part of the cleft of *syn*-**1**, whereas it moves towards more deep part of the cleft in the case of *syn*-**2**. This is also supported by NMR analysis.

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Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC 740154, 740155, 740157, 798876, 798877, 802620. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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18. The K value of the association constants is estimated from the following equation:

$$\Delta Abs = (L(1 + K\cdot X + K\cdot A)\text{-}((L^2(K\cdot X + K\cdot A + 1)^2 - 4K^2\cdot A\cdot X\cdot L^2)^{0.5}))/2K\cdot A$$

where X and A are $[\text{Guest}]_0$ and $[\text{Host}]_0$, respectively; L is ΔAbs at 100% complexation; L and K are treated as fitting parameters in the non-linear curve-fitting method.

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