(br d, $J = 5.1$ Hz, 1H), 3.60 (dddm, $J = 5.5$, 7.8, 8.4 Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ z, 2H), 5.30 (br ddd, $J = 5.5$, 7.8, 15.2 Hz, 1H), 5.39 (br dd, $J = 5.9$, 15.2 Hz, 1H), 7.16–7.32 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 14.1$, 20.9, 30.7, 35.3, 38.4, 40.5, 40.8, 44.1, 59.4, 70.2, 125.7, 125.8, 128.5, 133.1, 136.3, 140.3, 172.3 ppm; elemental analysis calcd for $C_{26}H_{36}O_5$: C 72.87, H 8.47; found: C 72.94, H 8.29.

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[9] The two isomers of **2** are apparently as a result of the relative configuration of the 1,5-stereogenic centers and not that of exocyclic double bonds. For example, PCC oxidation of a 7:1 mixture of **2e** provided the corresponding ketone as a single isomer, which furnished a 1:1 mixture of **2e** upon reduction with $NaBH_4$.

[10] CCDC-178844 contains the supplementary crystallographic data for this paper. These data can be obtained 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 deposit@ccdc.cam.ac.uk).

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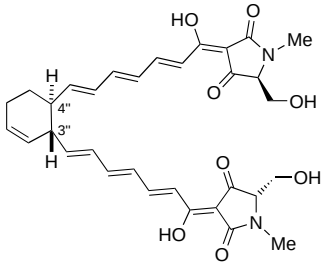
Total Synthesis of Polycephalin C and Determination of the Absolute Configurations at the 3″,4″ Ring Junction**

Deborah A. Longbottom, Angus J. Morrison, Darren J. Dixon, and Steven V. Ley*

Tetramic acids (2,4-pyrrolidinediones) are an important family of nitrogen-containing heterocycles, well known for their potent antibiotic, antiviral, antifungal, and cytotoxic activity.[1] Many tetramic acid natural products are highly complex frameworks containing several stereogenic centers. It is this complexity, together with the fact that these targets have potential or known biological activity, which makes their synthesis a worthwhile and challenging goal for the organic chemist, particularly so when the natural product is in short supply from the natural source.

In 1998, Nowak and Steffan isolated polycephalin C (**1**) as a new member of this group of natural products from *Physarum polycephalum*.[2] Polycephalin C (**1**) is a bis(trienoyltetramic acid), linked by an unusual asymmetric cyclohexene ring. The



polycephalin C (**1**)
showing unknown 3",4" absolute stereochemistry

tetramic acid unit of each terminus is derived from (*S*)-*N*-methyl serine and is linked by a fully conjugated *all-E*-triene chain to the cyclohexene ring. This unusual tetramic acid is thought to be one of several metabolites responsible for the yellow color of the wild-type plasmodia of *Physarum polycephalum*.[2]

Although the structure elucidation had established that the relative stereochemistry at the 3″,4″ ring junction of the natural product was *trans*, the absolute configuration at these positions had not been determined.[2] Therefore, intrigued by both the novel structure of this unusual polyenoyltetramic acid and the need to define the absolute stereochemistry at

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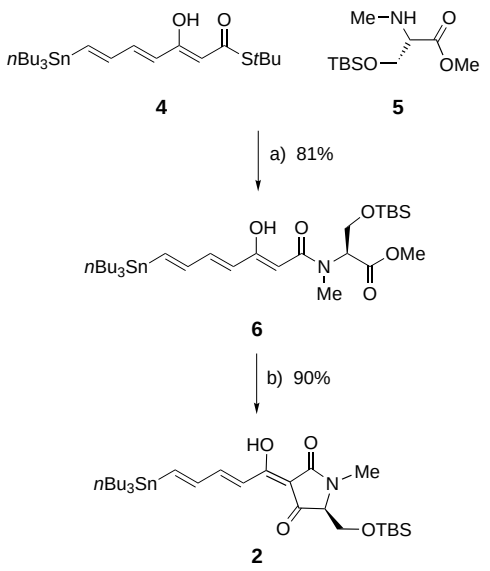
the 3″,4″ ring junction, we devised a synthesis route to the natural product.

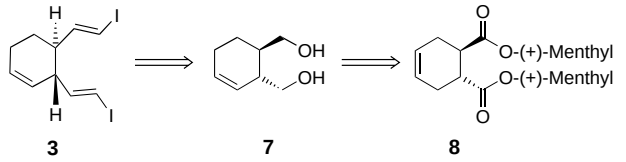
As the 3″,4″ ring junction configuration of polycephalin C (**1**) could be *R*,*R* or *S*,*S*, we arbitrarily selected the *S*,*S* isomer as the initial synthesis target. Analysis suggested a convergent approach, in which **1** is synthesized from two major fragments, the stannylated dienoyltetramic acid **2** and the bisiodovinyl intermediate **3** (Scheme 1). It was thought that **2** would be readily available from thioester **4** and amino ester **5**, fragments which had been devised and then used in the total synthesis of physarorubinic acid previously by our group.[3] Double Stille coupling to connect bisiodide **3** and tetramic acid **2**,[4] followed by TBS deprotection would then give polycephalin C (**1**) in a concise fashion. The synthesis of dienoyltetramic acid **2** is discussed first, followed by the synthesis of fragment **3** and the closing steps of the synthesis.

The two-step sequence which leads to the formation of dienoyltetramic acid **2** begins with a aminolysis reaction mediated by silver(ı) trifluoroacetate (Scheme 2).[5] In this particular case, it was found that an excess of triethylamine was crucial in preventing destannylation of the dienoylstannane **4**. Under these basic conditions, the silver-salt-mediated aminolysis reaction was complete after just 20 minutes at 0 °C and furnished the desired β-keto amide **6** in an excellent 81 % yield. Exposure of **6** to NaOMe in MeOH at 25 °C for two minutes then facilitated Lacey – Dieckmann cyclization which lead directly to dienoyltetramic acid **2** in a pleasing 90 % yield.[6]

With the tetramic acid portion of polycephalin C in hand, attention was focussed on the synthesis of the bisiodovinyl fragment **3**. It was envisaged that, starting from key intermediate cyclohexene diol **7**, 1,4-dioxidation and an unprecedented double Takai reaction[7] would provide the desired bisiodide **3** (Scheme 3). It was expected that diol **7** would be prepared from Diels – Alder adduct **8**; double-bond manipulation and exhaustive reduction would subsequently provide desired diol **7**.



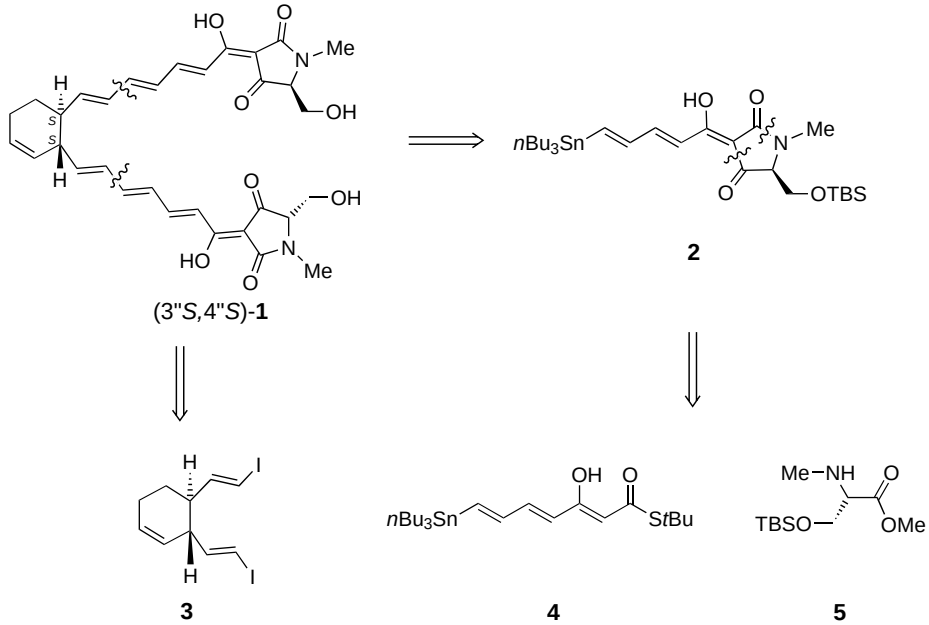
Scheme 2. Synthesis of dienoyltetramic acid **2**. a) CF_3CO_2Ag, NEt_3, THF, 0 °C, 20 min; b) NaOMe, MeOH, 25 °C, 2 min.



Scheme 3. Synthetic plan for bisiodovinyl fragment **3**.

The asymmetric Diels – Alder reaction employed in this case combines the dienophile, dimenthyl fumarate **9**, with 1,3-butadiene and is reported to occur with excellent diastereoselectivity.[8] Indeed in this case, the low-temperature Lewis acid mediated reaction proceeded to afford exclusively the desired Diels – Alder adduct (*R*,*R*)-**10** (d.e. > 95 % by NMR) in a 73 % yield (Scheme 4).

With the ring junction stereochemistry created in the Diels – Alder adduct **10**, double-bond transposition was then required. It was envisaged that overall addition of phenylselenic acid and a subsequent oxidation – elimination sequence would effect the desired process. Overall addition of phenylselenic acid to an alkene has been reported previously.[9] In this case, phenylselenium bromide in MeCN/water (15:1) facilitated smooth addition across the double bond of Diels – Alder adduct **10** and provided analytically pure hydroxyselenide **11** as the only diastereomer. *m*-CPBA oxidation of the phenylselenium moiety in the addition product **11** produced hydroxyselenoxide **12**, which then underwent elimination in the pres-



Scheme 1. Synthetic plan for polycephalin C (**1**). TBS = *tert*-butyldimethylsilyl.

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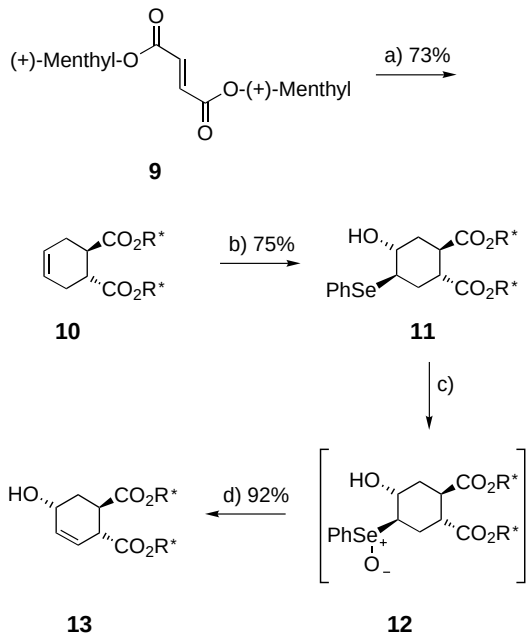
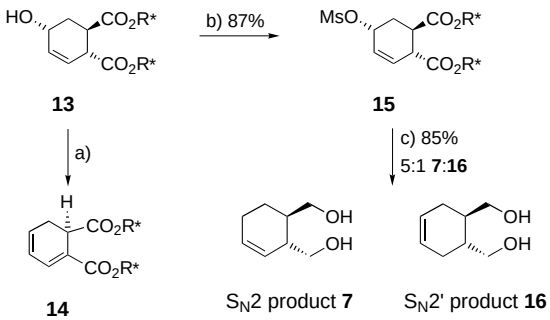


Scheme 4. Synthesis of allylic alcohol **13**. a) Et_2AlCl, 1,3-butadiene, $-60\,^{\circ}C$, 36 h; b) PhSeBr, $MeCN/H_2O$ (15:1), $50\,^{\circ}C$, 12 h; c) *m*-CPBA, CH_2Cl_2, $-30\,^{\circ}C$, 5 min; d) diisopropylamine, $50\,^{\circ}C$, 14 h. *m*-CPBA = *m*-chloroperoxybenzoic acid.

ence of diisopropylamine at $50\,^{\circ}C$ to generate allylic alcohol **13** in an excellent 92% yield (Scheme 4).

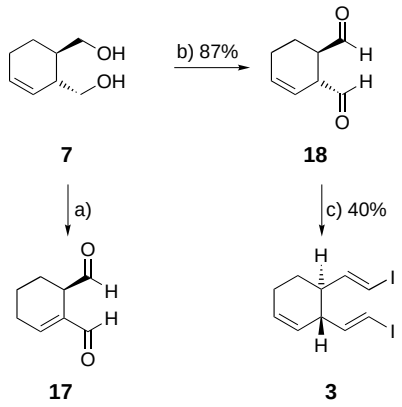
It was clear that the most efficient design of the synthesis would incorporate removal of the allylic hydroxy group with concomitant reduction of the (+)-menthyl esters. We believed that mesylation and subsequent exhaustive reduction would be effective. However, attempted mesylate formation at $0\,^{\circ}C$ was found to give diene **14** as the main product of the reaction (Scheme 5), formed by elimination of the mesylate immediately after formation. To prevent this side reaction, mesylate



Scheme 5. Synthesis of diol **7**. a) MsCl, NEt_3, CH_2Cl_2, $0\,^{\circ}C$; b) MsCl, NEt_3, CH_2Cl_2, $-78 \rightarrow -15\,^{\circ}C$; c) $LiAlH_4$, THF, $-78\,^{\circ}C \rightarrow RT$.

formation was therefore carried out at lower temperature and pleasingly provided the desired allylic mesylate **15**, the structure of which has been confirmed by X-ray crystallography.[10, 11] This was then used directly in the $LiAlH_4$ reduction of both esters and mesylate. The reduction led to an 85% yield of a separable mixture of diols **7** (product of direct S_N2 attack) and **16** (product of S_N2' attack) in a 5:1 ratio (Scheme 5), and provided a 71% yield of the desired diol **7**. By utilizing this synthetic sequence, gram quantities of diol **7** were accessed.

The 1,4-oxidation of diol **7** was then investigated and the Swern reaction selected as the optimum method.[12] Unfortunately, initial attempts gave α,β-unsaturated dialdehyde **17** (Scheme 6); the double bond had moved into conjugation



Scheme 6. Synthesis of bis-iodovinyl fragment **3**. a) $(COCl)_2$, DMSO, CH_2Cl_2, $-78\,^{\circ}C$, 2 h; then NEt_3, $-78 \rightarrow -10\,^{\circ}C$; b) $(COCl)_2$, DMSO, CH_2Cl_2, $-78\,^{\circ}C$, 1.5 h; then iPr_2NEt, $-78 \rightarrow -10\,^{\circ}C$; c) $CrCl_2$, CHI_3, THF, $0\,^{\circ}C \rightarrow RT$, 2 h.

with the proximal aldehyde as a result of the acidic nature of the allylic proton in the oxidation product **18**. However, this problem could be overcome by replacement of triethylamine with a more hindered base.[13] Thus, Swern oxidation with diisopropylethylamine, followed by a cold acidic workup and washing with a pH 7 buffer solution provided the desired aldehyde **18** in high yield and purity (Scheme 6). The unstable nature of this compound meant that it was always freshly prepared for immediate use in the subsequent step, formation of the Stille coupling partner **3**.

A double Takai olefination reaction[7] was selected to ensure the required *E* double-bond geometry in bisiodide **3**. However, because of the nonpolar nature of **3**, it was impossible to separate it from the residual excess of iodoform employed in the Takai reaction. Therefore, to obtain pure material for the Stille coupling, it was not possible to use an excess of iodoform, a constraint which led to a slightly disappointing but acceptable 40% yield considering the transformation which has been achieved (Scheme 6); the reaction was extremely selective for the desired product **3** (>90% bis-*trans* product by NMR) and hence the bisiodide **3** was formed from diol **7** in just two steps and overall 35% yield (Scheme 6).

A number of catalysts were then screened to ascertain which would facilitate the desired double Stille coupling in the most efficient manner, the best of which proved to be $[PdCl_2(CH_3CN)_2]$. Following optimization studies, the product **19** of the key double Stille coupling was successfully prepared in a good 53% yield (Scheme 7); two key bonds are formed in this reaction and, considering the possible palladium-mediated side reactions, this was an extremely pleasing outcome.

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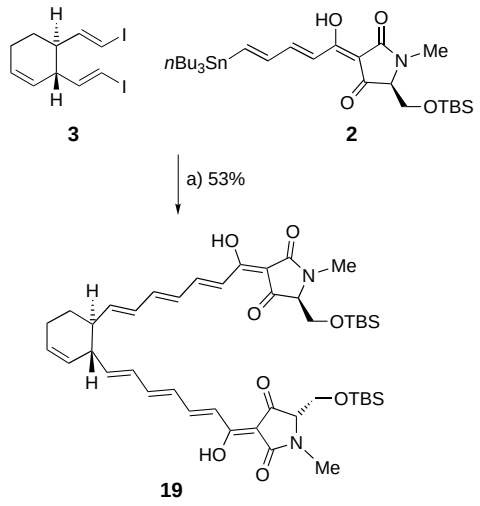
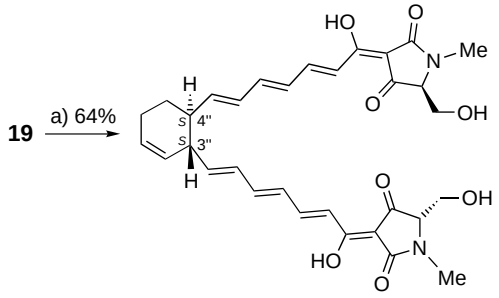


Scheme 7. Stille coupling of fragments **2** and **3**. a) $[PdCl_2(MeCN)_2]$ (15 mol %), DMF, RT, 1 h.

The final step of the synthesis, removal of the TBS ethers, was carried out with trifluoroacetic acid (TFA)/water (9:1) which facilitated smooth deprotection when added and immediately removed under reduced pressure (three times).[3a] Because all side products and excess reagents are volatile, crude **1** was afforded directly (Scheme 8), as no reaction workup was necessary. Purification by reverse-phase HPLC then gave (3″*S*,4″*S*)-**1** in 64 % yield and overall 3.7 % yield from dimenthyl fumarate **9**.

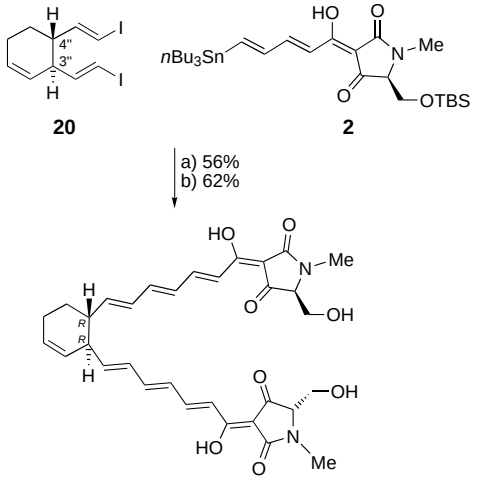


epi,*epi*-(3"*S*,4"*S*)-polycephalin C (**1**)

Scheme 8. Synthesis of *epi*,*epi*-(3″*S*,4″*S*)polycephalin C (**1**). a) TFA/H_2O (9:1) × 3, RT (64 %).

The spectroscopic data (^1H and ^{13}C NMR, MS, IR) of this synthetic material compared well with that published in the literature and the coupling constants from the polyene chains indicated the *all-E* double-bond geometry. However, despite being of the correct sign, the optical rotation was found to differ from that given in the structure elucidation paper.[2] The CD spectrum in the range from 300 to 450 nm was also different and from this it was concluded that the 3″*S*,4″*S*-configured compound was in fact *epi*,*epi*-(3″*S*, 4″*S*)-polycephalin C (Scheme 8) and that the isolated natural product had the *R*,*R* configuration about the ring junction.

To prove that this was correct, the synthesis had to be repeated beginning with (−)-dimenthyl fumarate to create the opposite configuration at the 3″,4″ ring junction. Synthesis of bis-iodovinyl fragment **20** proceeded uneventfully following the procedure outlined for **3**. Following Stille coupling with stannane **2**, deprotection gave polycephalin C (**1**), with 3″*R*,4″*R* stereochemistry at the ring junction (Scheme 9).



polycephalin C (**1**)
showing corrrect 3",4"-(*R*,*R*) absolute stereochemistry

Scheme 9. Synthesis of (3″*R*,4″*R*)-polycephalin C (**1**). a) $[PdCl_2(MeCN)_2]$ (5 mol %), DMF, RT, 1 h; b) TFA/H_2O (9:1) × 3, RT.

The spectroscopic data (^1H and ^{13}C NMR, MS, IR) of this synthetic material were in excellent agreement with that published in the literature and the coupling constants from the polyene chains again proved that the *all-E* double-bond geometry was intact. In this case the optical rotation and the CD spectrum, crucial for confirmation of configuration, were also in excellent agreement with the published data.

Thus, the total synthesis of this unusual bistetramic acid, polycephalin C (**1**), has been completed in a short and efficient fashion and the original challenge of defining the absolute configuration of the ring junction has been met. Through synthesis, we have been able to unambiguously assign the 3″*R*,4″*R* stereochemical configuration and thus complete the definition of the structure of this molecule.

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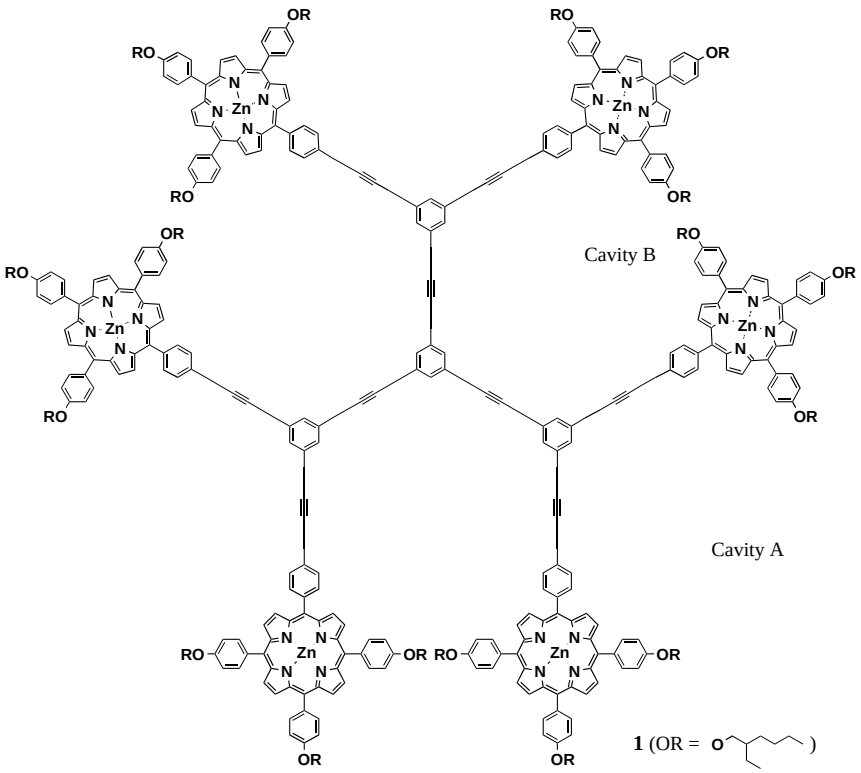

A Dendritic Porphyrin Receptor for C_{60} Which Features a Profound Positive Allosteric Effect

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The developmental investigation of the novel application of dendrimers and dendritic compounds has been of recent concern.[1] Dendrimers, as host molecules have attracted a great deal of attention because of their unique topology, well-defined structures, and unusual guest-binding behaviors compared to general polymers.[2] As [60]fullerene (C_{60}) exhibits outstanding new chemical and physical properties, the molecular design of C_{60} receptors is a growing research area.[3] For the crystal state, several articles have shown that porphyrin derivatives cocrystallize with C_{60} because of an attractive force between C_{60} and a porphyrin-ring center.[4] In organic solvents, Aida and co-workers[5] and Reed and co-workers[6] have shown that the porphyrin dimers have exceptionally high affinity for C_{60}. Herein, we describe a rigid star-shaped D_3-symmetric receptor **1**[7] bearing six porphyrin moieties linked with one another through phenylacetylene units. The dendritic receptor **1** has three rotational axes which affect the spatial arrangement of porphyrins (Figure 1), and the shape of the three clefts, each of which consists of two porphyrin planes. We have already demonstrated that the subunits for guest binding, which are rationally arranged around a rotational axis such as metal ion,[8] C–C bond,[9] or butadiynylene,[10] work cooperatively to bind guest molecules in a nonlinear fashion (positive homotropic allosterism). In addition, we have found that this effect is useful to bind guest molecules which are difficult to bind with a linear, 1:1 guest-binding fashion. As shown in Figure 1, when two porphyrins sandwich one C_{60} molecule, the complexation site successively suppresses the rotational freedom of the remaining porphyrin "tweezers". This "domino" effect is expected to be effective for the binding of three equivalents of C_{60} in an allosteric manner to attain high C_{60} affinity.

The formation of the **1**-C_{60} complex in toluene was indicated by a change in the UV/Vis absorption spectra induced by successive addition of C_{60} to **1** (Figure 2). The λ_{max} of the Soret band (428 nm) slightly shifts to longer wavelength (429 nm) with a tight isosbestic point (435 nm in Soret band region). The spectral characteristics are coincident with those of recent findings for a few porphyrin–C_{60} complexation systems.[5, 6]

To estimate the stoichiometry between **1** and C_{60}, ^{1}H NMR spectra for [**1**]:[C_{60}] = 1:0–1:5 at 25 °C were measured in [D_8]toluene ([**1**] = 0.50 mM). The resonance signals of the *meso*-aryl protons and β-pyrrole protons shifted upfield on C_{60} addition (see Supporting Information). As shown in Figure 3, a plot of $\Delta\delta$ versus [C_{60}]/[**1**] has a clear inflection point at [C_{60}]/[**1**] = 3.0. This value supports the view that the complex is

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