[23] **14** was prepared by reaction of 2-butyn-1,4-diol with 1.0 equiv *tert*-butyldimethylsilyl chloride and imidazole to form the mono-TBS protected derivative followed by reaction with triphenylphosphane and carbon tetrabromide.
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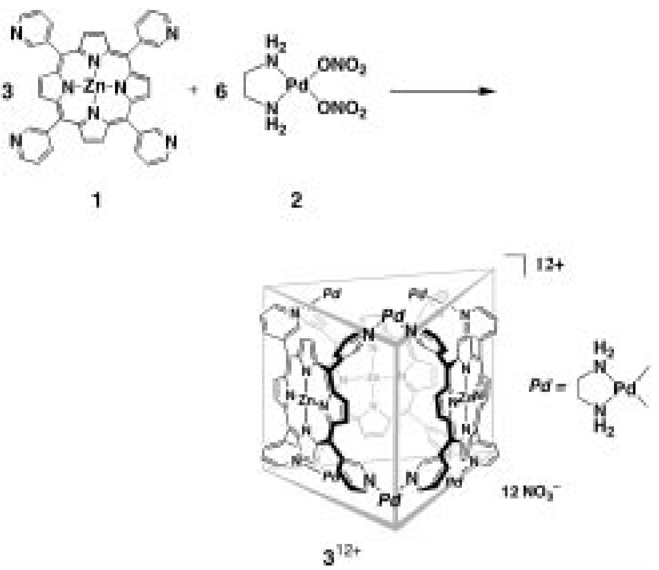
[29] Compounds **20** and **7** were characterized by high- and low-resolution mass spectra, respectively, in addition to ^{1}H NMR analysis.
[30] Computer-based modeling also predicts that glucofuranose should not form a stable complex with both boronic acid groups of **7**.
[31] Values of I_{rel} versus c were fitted to the equation $c = [(I_{\mathrm{rel}} - 1)/\Delta\varepsilon]/K\{[7]_{\mathrm{init.}} - (I_{\mathrm{rel}} - 1)/\Delta\varepsilon\} + (I_{\mathrm{rel}} - 1)/\Delta\varepsilon$ using Origin 5.0. The curves of Figure 2 were generated using B-spline fitting.
[32] The reported values are apparent dissociation constants as the reactions involve uptake or release of hydroxide ions on complex formation and dissociation, respectively, and the apparent equilibrium constants are thus pH dependent.[8]

A Porphyrin Prism: Structural Switching Triggered by Guest Inclusion**

Norifumi Fujita, Kumar Biradha, Makoto Fujita,*
Shigeru Sakamoto, and Kentaro Yamaguchi

Porphyrin assemblies play an essential role in biological systems for oxygen transport,[1] electron transfer, and energy migration and conversion.[2] In this regard, designing molecular assemblies with porphyrin units is a promising approach for constructing artificial functional systems. Both covalent[3] and noncovalent[4] syntheses of polyporphyrins have offered some novel classes of compounds with respect to their structures and functions. Here, we report a porphyrin-based hollow framework which is expected to open up a new area of porphyrin chemistry based on host–guest interactions. Our strategy employed here is the molecular paneling[5] of a pyridine-functionalized porphyrin by metal coordination. A prismlike hollow structure is quantitatively assembled from three porphyrin ligands and six $[\mathrm{Pd^{II}(en)}]^{2+}$ (en = ethylenediamine) building blocks (Scheme 1). The spatially fixed porphyrin ligands surround a large hydrophobic cavity which can accommodate neutral organic molecules, such as pyrene and perylene, in an aqueous solution. Though metal-linked porphyrinic square arrays have been reported by several groups,[6] the porphyrin cores in the arrays seem to adopt cofacial rather than perpendicular conformations and provide no distinct hollow structures capable of guest inclusion. Quite recently, a Pd$^{\mathrm{II}}$-linked porphyrin cage which bound diamines was reported by Shinkai and co-workers.[7]



Scheme 1. Self-assembly of porphyrin prism $\mathbf{3}^{12+}$.

The ligand designed here is the (3-pyridyl)-functionalized porphyrin **1**. This square panel-like ligand can be hinged by $[\mathrm{Pd^{II}(en)}]$ units at two opposite ridges of the square, and hence is anticipated to give a discrete porphyrin box structure.[8] Thus, the treatment of porphyrin ligand **1** with **2** (2 mol equiv) in H_2O/CH_3CN at 80 °C gave a purple homogeneous solution after one day. ^{1}H NMR spectroscopic analysis showed the formation of a single product, which was isolated as a violet precipitate in 96 % yield by adding acetone to the solution. After exchange of NO_3^- with PF_6^- ions, the structure of the product was assigned as $\mathbf{3}^{12+}$ by coldspray-ionization mass spectrometry (CSI-MS)[9] and NMR analyses. The CSI mass spectrum displayed prominent peaks corresponding to $[M - n(\mathrm{PF_6^-}) + m(\mathrm{CH_3CN})]^{n+}, (n = 3\text{–}9,\ m = 0\text{–}16)$[10] (see Supporting Information). Interestingly, one NO_3^- ion was not exchanged by an PF_6^- ion even when the complex was treated with a large excess of NH_4PF_6. The unexchanged NO_3^- ion was strongly trapped by the prism $\mathbf{3}^{12+}$. This was clearly evidenced by exact mass measurement.[11] For example, the highest peak at m/z 567.7613 (7^+ charge) corresponds to $[M - 6\,\mathrm{PF_6^-} - \mathrm{NO_3^-} + 7\,\mathrm{CH_3CN}]^{7+}$ (calcd 567.7561) and not

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[*] Prof. Dr. M. Fujita, Dr. K. Biradha
Department of Applied Chemistry
Graduate School of Engineering
Nagoya University
Furocho, Chikusaku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3199
E-mail: mfujita@apchem.nagoya-u.ac.jp

N. Fujita
The Graduate University for Advanced Studies
Myodaiji, Okazaki 444-8585 (Japan)

S. Sakamoto, Prof. Dr. K. Yamaguchi
Chemical Analysis Center, Chiba University
Yayoicho, Inageku, Chiba 263-8522 (Japan)

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

to $[M - 7\,PF_6^{-} + 5\,CH_3CN]^{7+}$ (calcd 567.8879), although both of them would show the same m/z value (568) by low resolution CSI-MS. The ^{1}H NMR spectrum fully agreed with the D_{3h} structure of $\mathbf{3}^{12+}$ with all-equivalent pyridyl groups and two inequivalent pyrrole units (singlets at $\delta = 9.01$ and 8.89; Figure 1).

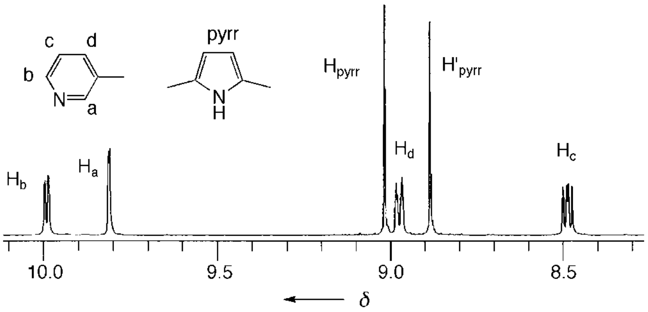
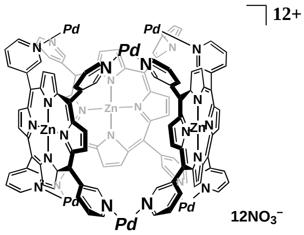
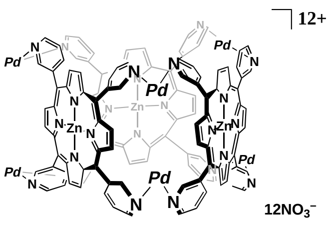


Figure 1. ^{1}H NMR spectrum (500 MHz, aromatic region) of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$ in D_2O/CD_3CN (1/1) at 300 K, 1.67 mM.

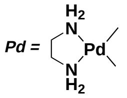
There are two possible conformations for the D_{3h} porphyrin prism structure: one with Pd centers at the apical positions of the prism (conformation **A**) and another one with the Pd centers at the equatorial positions (conformation **B**). Structural optimization of $\mathbf{3}^{12+}$ by using the Cerius^{2} program[12] revealed that **A** was more stable than **B** by 67.6 kcal mol^{-1}. In fact, conformation **A** was confirmed by an X-ray crystallographic analysis. A single crystal of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$ was obtained by slow diffusion of ethanol into an aqueous solution of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$ (8.3 mM) at 23 °C for one week. The crystal structure of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$ (Figure 2) clearly demonstrated that the three porphyrin-based ligands were hinged by six palladium atoms at the apical positions of the prism structure. The bite angles of Py-Pd-Py were close (83–91°) to the ideal value of 90°, while the pyridine rings were twisted by 48–73° with respect to the porphyrin planes. The shortest Pd ⋯ Pd distance was approximately 9 Å.



A



B



The D_{3h} conformation (**A**) of the prism dramatically changed upon the addition of pyrene, as monitored by NMR spectroscopy. Thus, powdered

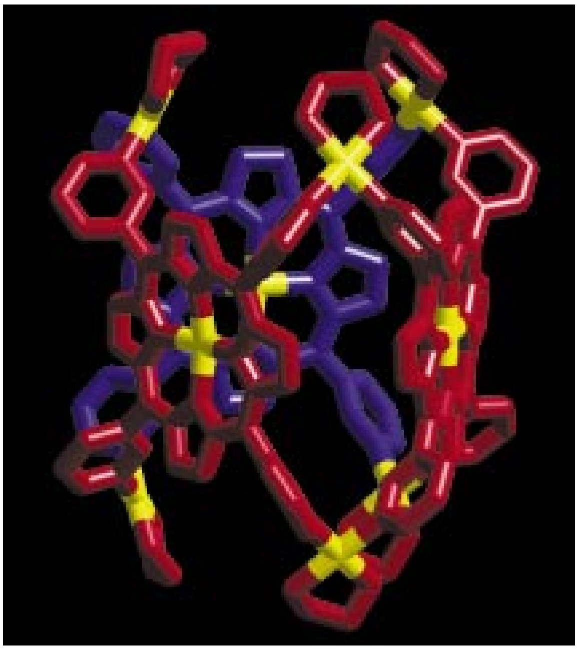


Figure 2. The X-ray crystal structure of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$. The water molecules on the Zn^{2+} centers are omitted for clarity.

pyrene (5 mol equiv) was suspended in the solution of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$ (1.67 mM in CD_3OD/D_2O (1/1)). After 3 h at 80 °C, the NMR spectrum became very complex (Figure 3) and suggests that guest binding triggered a desymmetrization of the prism structure. Interestingly, the guest molecule was not desymmetrized: the pyrene signals were observed at $\delta = 5.42$, 2.97, and 0.04 (see Supporting Information).[13] The large upfield shift of the guest signals is consistent with an inclusion of the pyrene in the cavity. The 1:1 host–guest ratio was clearly confirmed by NMR spectroscopy and CSI-MS.[14] A detailed analysis by 800 MHz NMR spectroscopy (^{1}H and HH-COSY; see Supporting Information) elucidated that the guest binding triggered the conformational change of the host from a D_{3h} to a C_2 symmetry. As shown in Figure 3, the twelve pyridyl groups in the prism were located in six different environments. Similarly, the twelve pyrrole rings were also

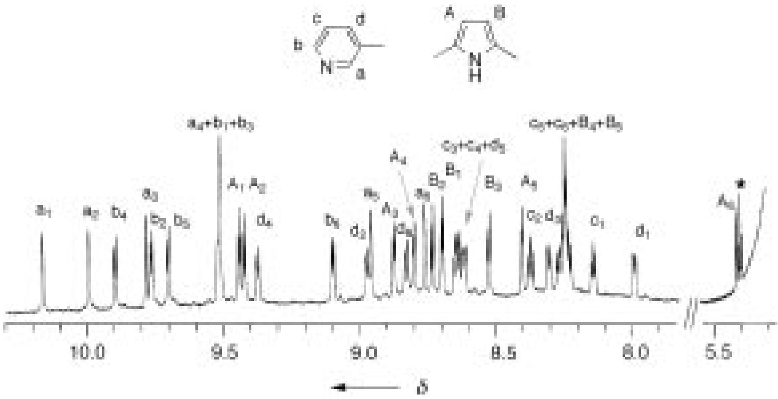


Figure 3. ^{1}H NMR (800 MHz) spectrum of the pyrene complex of $\mathbf{3}^{12+} \cdot 12\,NO_3^{-}$. The coupled pairs of pyrrole protons (A_1–B_1, A_2–B_2, …, A_6–B_6) were assigned. The B_6 proton is missing because of overlap with the H_2O signal at $\delta = 5.0$. Six correlated pairs b_1–c_1–d_1, b_2–c_2–d_2, …, b_6–c_6–d_6 were assigned for the 3-Py protons, while correlations with a_1–a_6 were not assigned. The * denotes the pyrene resonances.

located in six different environments, where each pyrrole was desymmetrized. These NMR observations fully agree with the C_2 symmetry.

We suggest that the guest binding triggered the apical-to-equatorial flipping of two Py-Pd-Py hinges at a diagonal position, thus providing C_2-symmetrized conformation **C** (Figure 4). This transformation was strongly supported by a refinement using the Cerius^2 program. Two porphyrin faces are almost parallel to each other in the refined conformation **C** with an interplane distance of approximately 7.1 Å, which is an ideal distance to bind an aromatic ring in the cavity. The conformational change was also triggered by other large aromatic guests such as perylene and triphenylene. Small aromatic compounds such as benzene were also included by **3**, but the host conformation was not changed.

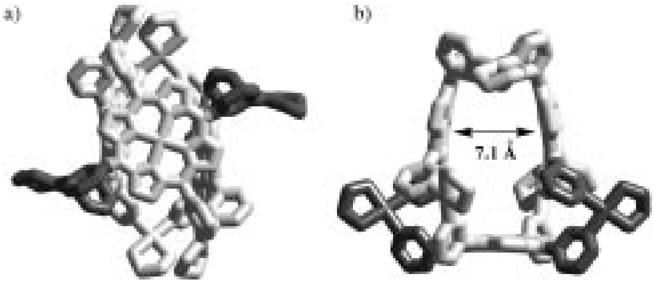


Figure 4. Optimized structure of the pyrene complex of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ (conformation **C**): a) side view and b) top view. The pyrene molecule exists inside the cavity, but is omitted for clarity.

The UV/Vis spectrum of the pyrene complex of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ shows the Q-band to be dramatically red-shifted by about 13 nm relative to the empty prism $\mathbf{3}^{12+}\cdot 12\,NO_3^-$. This observation suggests that there is a strong π–π interaction between the aromatic rings of the host and the guest molecules. Photophysical properties are currently under investigation.

Experimental Section

$\mathbf{3}^{12+}\cdot 12\,NO_3^-$: Zinc 5,10,15,20-tetra(3-pyridyl)-21*H*,23*H*-porphyrin (**1**; 1.10 g, 1.62 mmol) was treated with $[Pd(en)(NO_3)_2]$ (**2**; 0.939 g, 3.23 mmol) in a mixture of water and acetonitrile (1/1, 324 mL) at 80 °C for 1 day. The addition of acetone (2.5 L) to the resulting purple solution precipitated a purple powder which was separated by centrifugation and dried in vacuo to give $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ (1.95 g, 0.515 mmol, 96 %). M.p. >480 °C; ^{1}H NMR (500 MHz, CD_3CN/D_2O (1/1)): $\delta = 9.99$ (d, $J = 5.7$ Hz, 12 H), 9.81 (s, 12 H), 9.01 (s, 12 H), 8.97 (d, $J = 8.1$ Hz, 12 H), 8.89 (s, 12 H), 8.49 (dd, $J = 8.1$, 5.7 Hz, 12 H), 3.56–3.51, 3.48–3.42 (m, 24 H); ^{13}C NMR (125 MHz, CD_3CN/D_2O (1/1)): $\delta = 153.856$ (CH), 150.585 (CH), 149.439 (Cq), 149.226 (Cq), 144.948 (CH), 141.199 (Cq), 131.944 (CH), 131.510 (CH), 124.940 (CH), 114.231 (Cq); IR (KBr): 1578, 1364, 1192, 1059, 995, 797, 718 cm^{-1}; UV/Vis (H_2O) λ_{max} (ε [cm^{-1}M^{-1}]): 322 (49460), 422 (424600), 561 (31200), 601 nm (9620). An aqueous solution of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ (100 mg, 0.026 mmol in 40 mL of water) was poured into an aqueous solution of saturated NH_4PF_6. The violet precipitate was separated by centrifugation, washed with water three times, and then dried in vacuo to give $\mathbf{3}^{12+}\cdot 11\,PF_6^-\cdot NO_3^-$ (102 mg, 0.021 mmol, 81 %). Elemental analysis (%) calcd for $C_{122}H_{120}F_{66}N_{37}O_3P_{11}Pd_6Zn_3\cdot 23\,H_2O$: C 30.99, H 3.27, N 10.13; found: C 30.86, H 2.89, N 9.79.

Crystal data for $\mathbf{3}^{12+}\cdot 12\,NO_3^-$: The single crystal of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ was prepared by the slow diffusion of ethanol into an aqueous solution of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$ (8.3 mM) at 23 °C for 1 week. Triclinic, space group $P\bar{1}$, $a = 20.6267(14)$, $b = 20.7442(14)$, $c = 28.1631(19)$ Å, $\alpha = 72.8840(10)$, $\beta = 74.0620(10)$, $\gamma = 66.2070(10)°$, $V = 10\,369.3(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.452$ g cm^{-3}, 23102 unique reflections out of 36032 with $I > 2\sigma(I)$, $1.10 < \theta < 25.00°$, final R factors $R_1 = 0.1068$, $wR_2 = 0.2985$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157344. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] Using CH_3CN as the solvent enhanced the peak intensities in the CSI-MS study, probably because of its effective solvation of the cationic core which facilitated the separation of the PF_6^- counterions.

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[14] CSI-MS data of the pyrene complex of $\mathbf{3}^{12+}\cdot 12\,NO_3^-$: CSI-MS ($CH_3CN/H_2O$ (1/1)) m/z: 1267.9 $[\mathbf{3}^{12+}-3\,NO_3^-+\text{pyrene}]^{3+}$, 935.4 $[\mathbf{3}^{12+}-4\,NO_3^-+\text{pyrene}]^{4+}$, 736.0 $[\mathbf{3}^{12+}-5\,NO_3^-+\text{pyrene}]^{5+}$, 603.3 $[\mathbf{3}^{12+}-6\,NO_3^-+\text{pyrene}]^{6+}$ (see the Supporting Information). Pyrene seems to be strongly entrapped within the cavity of $\mathbf{3}^{12+}$ since **3**–pyrene species were clearly observed by CSI-MS.

Preparation and Properties of Polymer-Wrapped Single-Walled Carbon Nanotubes**

Alexander Star, J. Fraser Stoddart,* David Steuerman, Mike Diehl, Akram Boukai, Eric W. Wong, Xin Yang, Sung-Wook Chung, Hyeon Choi, and James R. Heath*

Since the discovery[1] of single-walled carbon nanotubes (SWNTs) in 1993, it has become increasingly apparent that SWNTs, on account of their novel, structural, mechanical, and electronic properties, constitute a form of carbon with potential applications in many fields.[2] The remarkable electronic properties of SWNTs render them attractive candidates[2, 3] for use as the wiring components for nanoscale devices and circuitry. Many SWNT-based devices, such as field-effect transistors[3] and chemical sensors,[4] have been demonstrated. One major problem—from the standpoint of manipulating and processing SWNTs—is the insolubility of SWNTs in all solvents. Although considerable progress has been made on the open-end[5, 6] and side-wall[7] modifications of SWNTs using covalent chemistry, it has so far not been possible to establish an efficient means of handling and manipulating NTs without risking their partial destruction. Thus, it seems attractive to explore supramolecular approaches, that is, noncovalent modifications, since 1) they will not disrupt the extended π networks of SWNTs and 2) they could open up the possibilities of being able to organize NTs into ordered networks.

Molecules of high molecular weight that can either thread themselves onto or wrap themselves around the surfaces of SWNTs have attracted our attention as potential noncovalent modifiers of NTs that could disrupt the van der Waals interactions that cause SWNTs to aggregate into bundles. Polymers are appealing candidates to host the complexation of SWNTs since, given an appropriate structure, they can wrap themselves around SWNTs. Indeed, polymer–NT materials have been reported.[8] Composite materials based on conjugated luminescent polymers, such as poly(metaphenylenevinylene) (PmPV), filled with NTs exhibit[9] properties which are enhanced relative to those of the individual components. For example, NT/PmPV composites have exhibited nearly eightfold increases in electrical conductivity compared with just the polymer, and without impairment of the photo- and/or electroluminescence properties of the polymer.[9] Here we report on an efficient synthesis of a substituted PmPV, followed by the characterization of SWNT/PmPV′ complexes using UV/Vis and ^1H NMR spectroscopies. We then utilize AFM, optical, and electronic measurements of single, isolated SWNT/PmPV′ structures as a means to analyze quantitatively these systems.

Our preparation of the substituted PmPV[10] is summarized in Scheme 1. We have found that SWNTs can be suspended in solutions of PmPV′ in $CHCl_3$. The UV/Vis absorption spectra (Figure 1) were obtained from a dilute solution (0.06 mg mL^{-1}) of the polymer and the SWNT/PmPV′ complex in $CHCl_3$. Two major absorption bands were observed for PmPV′, with λ_{max} values of 329 and 410 nm. These bands broaden in the complex, presumably as a result of π–π interactions between the SWNTs and the fully conjugated PmPV′ backbone. Moreover, the SWNT/PmPV′ complex yields a spectrum with broad absorptions around 650 and 900 nm. These wavelengths correspond roughly to the band-to-band transitions of pure SWNTs.[7c] While the polymer is bright yellow, the complex possesses a deep green color. The ^1H NMR (360 MHz, $CDCl_3$) spectrum of the SWNT/PmPV′ complex reveals (Figure 2a) significant broadening and small shifts in the resonances for the protons on the polymer, and even the TMS standard is broadened. This broadening arises most likely from the presence of conducting SWNTs, as well as from the presence of the ferromagnetic particles that are catalysts for the SWNT synthesis. Nevertheless, this broadening is not

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[*] Prof. J. F. Stoddart, Prof. J. R. Heath, Dr. A. Star, D. Steuerman, M. Diehl, A. Boukai, Dr. E. W. Wong, Dr. X. Yang, S.-W. Chung, Dr. H. Choi
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-1843
E-mail: stoddart@chem.ucla.edu, heath@chem.ucla.edu

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