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Sensing of Chiral Fullerenes by a Cyclic Host with an Asymmetrically Distorted π-Electronic Component

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Design of host molecules for recognizing asymmetrically distorted π-electronic surfaces of carbon nanoclusters is one of the most challenging issues in relation to the discrimination of metallic and semiconducting carbon nanotubes.[1] Unlike ordinary asymmetric compounds, carbon nanoclusters are devoid of any appropriate functionalities for point recognition so that their chirality sensing certainly requires a different strategy. Here we report a novel heterocyclic porphyrin dimer ($\mathbf{1_{Rh}}$, Chart 1), containing an asymmetrically distorted *N*-alkylporphyrin as the first host molecule capable of sensing chiral fullerene C_{76} by means of ^{1}H NMR. Chiral fullerenes such as C_{76}, C_{78}, and C_{84}[2] are all-carbon spheroidal clusters, and designing of sensing hosts for these discrete chiral objects would give a new rationale for the recognition of asymmetrically curved π-electronic surfaces.

Newly designed cyclic host $\mathbf{1_{Rh}}$ bears a C_1-symmetric *N*-methyldiarylporphyrin ($\mathbf{P_{NMe}}$) moiety on the other side of a methylrhodium diarylporphyrin ($\mathbf{P_{Rh}}$) unit. *N*-Alkylporphyrins are nonplanar because porphyrins cannot sterically accommodate *N*-alkyl groups in their nitrogen core. Thus, as reported previously,[3] *N*-alkylporphyrins are chiral depending on the arrangement of the peripheral substituents, and their enantiomers are separable by means of chiral HPLC. We chose $\mathbf{P_{Rh}}$ as the counterpart of this chiral porphyrin, because cyclic dimers of methylrhodium porphyrins can accommodate fullerenes to form highly stable inclusion complexes.[4b,c,f] The molecular design of $\mathbf{1_{Rh}}$ was based on an expectation that the asymmetrically distorted π-electronic surface of $\mathbf{P_{NMe}}$ could fit those of chiral fullerenes trapped in the $\mathbf{P_{Rh}}$-containing host cavity. A racemic mixture of $\mathbf{1_{Rh}}$ (($\pm$)-$\mathbf{1_{Rh}}$) was obtained by alkaline-mediated coupling of a *N*-methylporphyrin bearing bromoalkyl pendants with a methylrhodium porphyrin having phenolic functionalities and unambiguously characterized by MALDI-TOF-MS and ^{1}H NMR analyses.[5] Optical resolution of $\mathbf{1_{Rh}}$ was achieved by preparative chiral HPLC on CHIRALPAK IA with hexane/CH_2Cl_2/Et_2NH (87.5/12.5/0.1, v/v/v) as an eluent,[5] where the two well-separated fractions showed mirror-image circular dichroism (CD) spectra of one another (Figure 1a). The first and second fractions displayed the most intensive CD bands at 420 nm, with negative and positive signs, respectively, and are denoted as ($-$)-$\mathbf{1_{Rh}}$ and (+)-$\mathbf{1_{Rh}}$. As a metal-free reference of $\mathbf{1_{Rh}}$, we synthesized $\mathbf{1_{2H}}$ (Chart 1) and successfully separated its enantiomers ($-$)-$\mathbf{1_{2H}}$ and (+)-$\mathbf{1_{2H}}$ by preparative chiral HPLC (Figure 1b).[5] As the guest fullerene, C_{76} was chosen for simplicity because other chiral fullerenes, unlike C_{76}, possess more than two geometrical isomers.[2]

Host $\mathbf{1_{Rh}}$ can include C_{76} in its cavity. Spectroscopic titration of ($\pm$)-$\mathbf{1_{Rh}}$ with ($\pm$)-C_{76} in toluene at 20 °C resulted in a decrease in absorbances at 423 and 406 nm due to $\mathbf{P_{NMe}}$ and $\mathbf{P_{Rh}}$, respectively,[5] indicating that the two porphyrin moieties in $\mathbf{1_{Rh}}$ both interact with C_{76}. From the absorbance changes at 423 and 406 nm, association constants (K_{assoc}) of 1.5×10^7 and 1.4×10^7 M^{-1}, virtually identical to one another, were obtained, respectively. Similar to cyclic dimers of other porphyrins, ($\pm$)-$\mathbf{1_{Rh}}$ alone in toluene-d_8 at 20 °C showed multiple ^{1}H NMR signals due to, for example, the *N*-Me ($\delta = -4.61$ to -4.95 ppm) and RhMe ($\delta = -6.07$ to -6.54 ppm) groups because of the presence of conformational isomers.[4,5] However, upon mixing ($\pm$)-$\mathbf{1_{Rh}}$ with an equimolar amount of ($\pm$)-C_{76}, the ^{1}H NMR spectrum became much simplified, displaying single signals due to the *N*-Me and RhMe groups at downfield regions, $\delta = -4.57$ and -5.82 ppm, respectively.[5] Molecular models predicted that better fitting of the π-electronic cavity of $\mathbf{1_{Rh}}$ to C_{76} requires unfavorable conformational isomers of $\mathbf{1_{Rh}}$ to rotate $\mathbf{P_{NMe}}$ and $\mathbf{P_{Rh}}$ to point their *N*-Me and RhMe groups outward. At a closer look, one may notice that the NH proton of $\mathbf{P_{NMe}}$ shows two split signals at $\delta = -2.76$ and -2.79 ppm (Figure 2a). When (+)-C_{76} was allowed to complex with ($-$)-$\mathbf{1_{Rh}}$ and (+)-$\mathbf{1_{Rh}}$ under identical conditions to the above, either of the two NH signals was observed. Hence, the characteristic signals at δ -2.76 and -2.79 ppm are assignable to diastereoisomers ($-$)-$\mathbf{1_{Rh}}\supset$(+)-C_{76}/(+)-$\mathbf{1_{Rh}}\supset$($-$)-C_{76} and (+)-$\mathbf{1_{Rh}}\supset$(+)-C_{76}/($-$)-$\mathbf{1_{Rh}}\supset$($-$)-C_{76}, respectively. We confirmed that the integral ratio of these two signals remains unity, even upon increment of the guest/host ratio from 1 up to 4.[5] Therefore, chiral

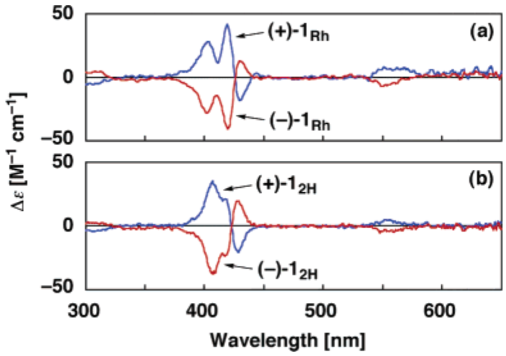
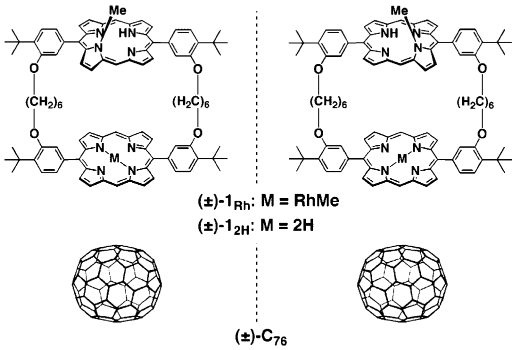


Figure 1. CD spectra of the enantiomers of (a) $\mathbf{1_{Rh}}$ (($-$)-$\mathbf{1_{Rh}}$ and (+)-$\mathbf{1_{Rh}}$) and (b) $\mathbf{1_{2H}}$ (($-$)-$\mathbf{1_{2H}}$ and (+)-$\mathbf{1_{2H}}$) in toluene at 20 °C.

Chart 1



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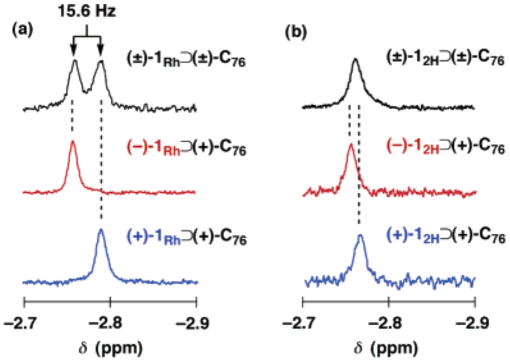

Figure 2. ^{1}H NMR (500 MHz) spectra (NH signals of $\mathbf{P_{NMe}}$) of equimolar mixtures of (+)-host/(+)-C_{76} (blue curves), (−)-host/(+)-C_{76} (red curves), and (±)-host/(±)-C_{76} (black curves) in toluene-d_8 at 20 °C. Host = (a) $\mathbf{1_{Rh}}$ and (b) $\mathbf{1_{2H}}$. [(+)-C_{76}] = [(±)-C_{76}]/2 = 7.7×10^{-5} M.

cyclic host $\mathbf{1_{Rh}}$ is nonenantioselective in the guest binding but can spectroscopically discriminate the enantiomers of C_{76}.

The $\mathbf{P_{Rh}}$ unit as well as the chiral $\mathbf{P_{NMe}}$ moiety of $\mathbf{1_{Rh}}$ contributes to the chiral discrimination of C_{76}. Metal-free reference $\mathbf{1_{2H}}$, upon titration with C_{76} in toluene at 20 °C, displayed an absorption spectral change similar to that observed for $\mathbf{1_{Rh}}$, where K_{assoc} obtained for $\mathbf{1_{2H}}\supset C_{76}$ (2.5×10^6 M^{-1}) was an order of magnitude smaller than that for $\mathbf{1_{Rh}}\supset C_{76}$.[5] While the inclusion complexation of (±)-$\mathbf{1_{2H}}$ with (±)-C_{76} in toluene-d_8 at 20 °C showed an analogous ^{1}H NMR spectral change profile to that of (±)-$\mathbf{1_{Rh}}$ with (±)-C_{76}, none of the characteristic signals due to the *N*-Me and NH groups of $\mathbf{P_{NMe}}$ displayed diastereoisomeric splitting (Figure 2b).[5] We then lower the temperature for the measurement down to −20 °C. Although the NH signal of $\mathbf{P_{NMe}}$ remained single, the *N*-Me signal started to split at −10 °C into two signals.[5] Hence, metal-free $\mathbf{1_{2H}}$ is not as practical as $\mathbf{1_{Rh}}$ for the chirality sensing of C_{76}. This is due to the coalescence of diastereoisomerically split signals caused by the dynamics in guest exchange of (−)-C_{76} with (+)-C_{76}, because the combination of enantiomerically pure $\mathbf{1_{2H}}$ and C_{76}, that is, (−)-$\mathbf{1_{2H}}\supset$(+)-C_{76} and (+)-$\mathbf{1_{2H}}\supset$(+)-C_{76}, gave signals with different chemical shifts both for the *N*-Me and for the NH groups at 20 °C (Figure 2b).[5] By ^{1}H NMR line-shape analysis on an equimolar mixture of (−)-$\mathbf{1_{2H}}$ and (±)-C_{76} with a program DNMR5,[4c,f] the guest-exchange rate constant between (−)-$\mathbf{1_{2H}}\Delta$(−)-C_{76} and (−)-$\mathbf{1_{2H}}\supset$(+)-C_{76}, evaluated in regard to the NH resonance of $\mathbf{P_{NMe}}$, was 35 s^{-1} at 20 °C. As expected from the large affinities of cyclic dimers of rhodium porphyrins toward fullerenes,[4b,c,f] ^{1}H NMR line-shape analysis on an equimolar mixture of (−)-$\mathbf{1_{Rh}}$ and (±)-C_{76} gave a guest-exchange rate constant of 1 s^{-1}, much smaller than that with (−)-$\mathbf{1_{2H}}$.

Thanks to the good resolution of the diastereoisomerically split NH signals (15.6 Hz) of $\mathbf{1_{Rh}}\supset C_{76}$ (Figure 2a), the enantiomers of cyclic host $\mathbf{1_{Rh}}$ can be used for the accurate determination of the optical purity of C_{76}. As shown in Figure 3a, the integral ratio of the split NH signals of $\mathbf{P_{NMe}}$ in (−)-$\mathbf{1_{Rh}}\supset C_{76}$ is entirely dependent on the $\Delta\epsilon$ value of C_{76}. Plots of the enantiomeric purities of guest C_{76}, as determined by the integral ratio of the NH signals of $\mathbf{P_{NMe}}$ in (−)-$\mathbf{1_{Rh}}\supset C_{76}$, versus the $\Delta\epsilon$ values of C_{76} gave a linear correlation. Extrapolation of the fitted line of the plots to the enantiomeric purity of 100% (Figure 3b) provided an absolute $\Delta\epsilon$ value of 58.5 M^{-1} cm^{-1} for enantiomerically pure C_{76} in toluene at 330 nm. This value is larger than those obtained so far via direct chiral HPLC separation (14.3 M^{-1} cm^{-1})[6c] or methods involving chemical transformations (8.9 and 53.4 M^{-1} cm^{-1}).[6a,b]

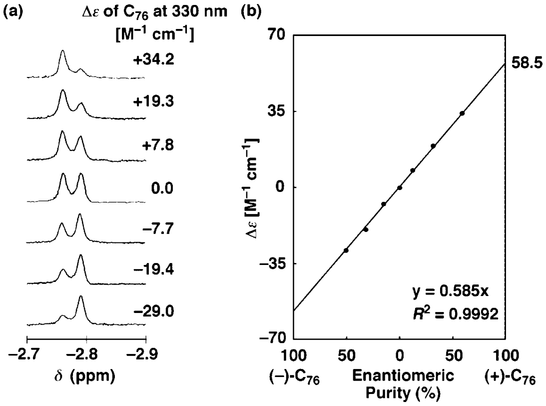

Figure 3. (a) ^{1}H NMR (500 MHz) spectra (NH signals of $\mathbf{P_{NMe}}$) of equimolar mixtures of (−)-$\mathbf{1_{Rh}}$ and C_{76} of different $\Delta\epsilon$ values ([C_{76}] = 1.5 × 10^{-4} M) in toluene-d_8 at 20 °C. (b) Plots of enantiomeric purities of C_{76}, as determined by the integral ratio of the NH signals of (−)-$\mathbf{1_{Rh}}\supset C_{76}$, versus $\Delta\epsilon$ values of C_{76} in toluene at 20 °C.

In conclusion, by using a C_1-symmetric *N*-methylporphyrin as an asymmetrically distorted π-electronic component, we have developed the first chiral host $\mathbf{1_{Rh}}$ capable of discriminating the enantiomers of C_{76} by means of ^{1}H NMR and also determining its enantiomeric purity by visualization of the relative enantiomeric abundance. By virtue of this direct method, an accurate $\Delta\epsilon$ value of enantiomerically pure C_{76} has been obtained. Elaboration of the obtained rationale into the molecular design of host molecules for enantiomeric separation of chiral fullerenes and larger carbon nanoclusters is one of the subjects worthy of further investigation.

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Supporting Information Available: Synthesis and optical resolution of $\mathbf{1_{Rh}}$, $\mathbf{1_{2H}}$, and C_{76} and analytical data of mixtures of $\mathbf{1_{Rh}}$ or $\mathbf{1_{2H}}$ with C_{76}. This material is available free of charge via the Internet at http://pubs.acs.org.

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