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A novel [60]fullerene receptor with a Pd(II)-switched bisporphyrin cleft

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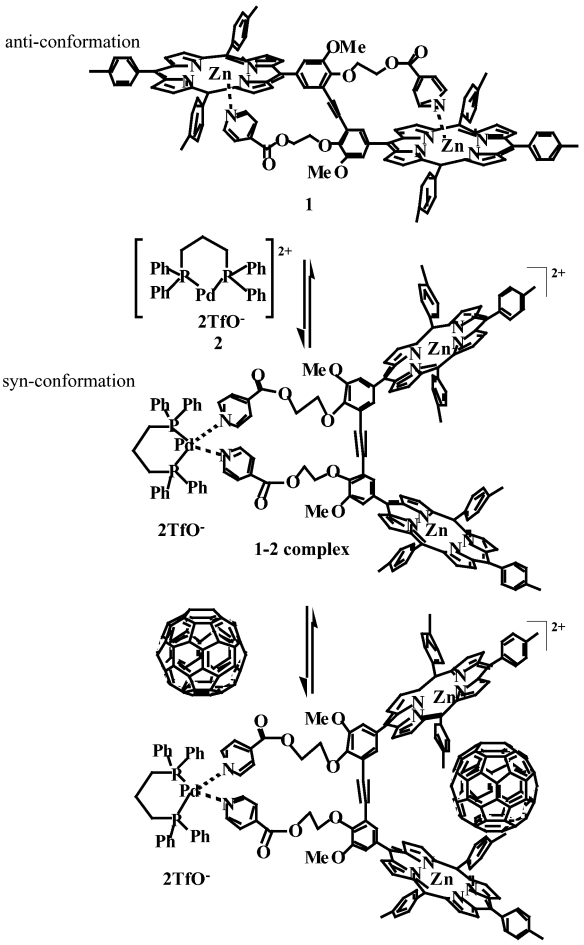
Porphyrin dimer 1, which does not have an inside cavity and cannot interact with [60]fullerene (C_{60}), becomes an excellent C_{60}-acceptor with a large cavity in the presence of a Pd(II) complex.

The development of new host molecules for fullerenes has received much attention to dissolve them in solution or to add new physical and chemical functions to them.[1] Especially, several diad systems consisting of porphyrin–fullerene conjugates[2] have drawn particular attention because of their significant future potential; photoinduced electron-transfer occurs efficiently and the charge separated state is preserved more stably than those in other nonfullerene diad systems.[3] In the crystal state, several articles have shown that porphyrin derivatives cocrystallize with [60]fullerene (C_{60}) owing to an attractive force between C_{60} and a porphyrin ring centre.[4] In organic solvents, Aida and coworkers[5] and Reed and coworkers[6] have shown that the porphyrin dimers have exceptionally high affinity with C_{60}. It thus occurred to us if one can design such a porphyrin dimer that is interconverted between the 'on' state and the 'off' state by a switch function,[7] the resultant molecular receptor should control the various C_{60} functions by a trigger. Here, we report porphyrin dimer **1** which has, within a molecular, two pyridyl moieties acting as a switch through the interaction with Pd(II) complex **2**. Very interestingly, we have found that this **1**–**2** complex can include C_{60} only in the 'on' state in the presence of **2** (Scheme 1).

As shown in Fig. 1(a), a simple ^{1}H NMR splitting pattern was obtained for **1**† in toluene-d_8:CD_2Cl_2 = 50:1 (v/v), indicating that this molecule adopts a symmetrical structure. Peaks for the α- and β-protons in the pyridyl groups of **1** are observed in higher magnetic field (2.50 and 5.69 ppm, respectively), suggesting that the pyridyl groups act as axial ligands to bind Zn(II) and these proton signals are shifted by the strong shielding effect of the porphyrin systems (Scheme 1). The molecular weight of **1** was estimated to be *ca.* 2000 ± 150 by gel permeation chromatography (GPC) in $CHCl_3$, showing that the pyridine–Zn(II) interaction is an intramolecular event. When **1** and **2** were mixed in toluene-d_8:CD_2Cl_2 = 50:1 (v/v), a simple ^{1}H NMR splitting pattern was obtained again at the [**1**]:[**2**] = 1:1 ratio (Fig. 1(c)). Large downfield shifts are observed for the α- and β-protons in the pyridyl groups of **1** (9.51 and 7.73 ppm, respectively). These chemical shift changes are ascribed to a structural change from intramolecular pyridine–Zn(II) interactions to intermolecular pyridine–Pd(II) interactions. These results consistently support the view that by the addition of Pd(II) complex **2**, the intramolecularly-bridged *anti*-conformation is transformed to the *syn*-conformation (as shown in Scheme 1). When the ratio was changed to 2:1 ([**1**]:[**2**]), the ^{1}H NMR spectrum gave two sets of peaks, separately, assignable to **1** and the **1**–**2** complex (Fig. 1b). The result shows that the complexation–decomplexation exchange rate is slower than the ^{1}H NMR time-scale. The relative peak intensities for **1** and the **1**–**2** complex support the formation of a 1:1 complex between **1** and **2** in solution.

To obtain further insights into the structures of **1** and the **1**–**2** complex, we also measured the UV–vis absorption and mass



Scheme 1

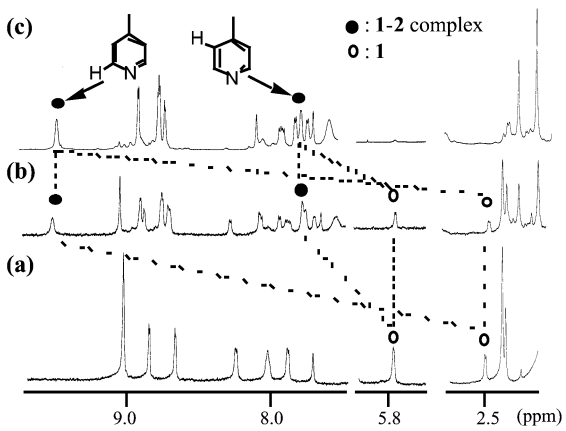


Fig. 1 ^{1}H NMR spectra of (a) **1**, (b) [**1**]:[**2**] = 2:1 and (c) [**1**]:[**2**] = 1:1 in toluene-d_8:CD_2Cl_2 = 50:1 (v/v) at 25 °C: [**1**] = 1.0 × 10^{-3} M.

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spectra. Fig. 2 shows the influence of added **2** on the absorption spectral change of **1** (25 °C, toluene : CH_2Cl_2 = 50 : 1 (v/v)). It is seen from Fig. 2 that λ_{max} for the Soret band (432.5 nm) shifts to shorter wavelength (424 nm) with a tight isosbestic point (428 nm in the Soret band region). It is evident, therefore, that the coordination bonds change from pyridine–Zn(II) to pyridine–Pd(II). From a plot of ΔA_{432} *vs.* [**2**] (insert in Fig. 2), one can obtain $K = 3.7 \times 10^4$ M^{-1} for the formation of the 1 : 1 complex from **1** and **2**. Moreover, the formation of the **1–2** complex was also supported by coldspray ionization mass spectrometry (CSI MS). The CSI MS spectrum[8] shows a strong peak at *m/z* 2518.13 for $[\mathbf{1}\cdot\mathbf{2} - CF_3SO_3^-]^+$, proving the formation of a 1 : 1 complex from **1** and **2**.

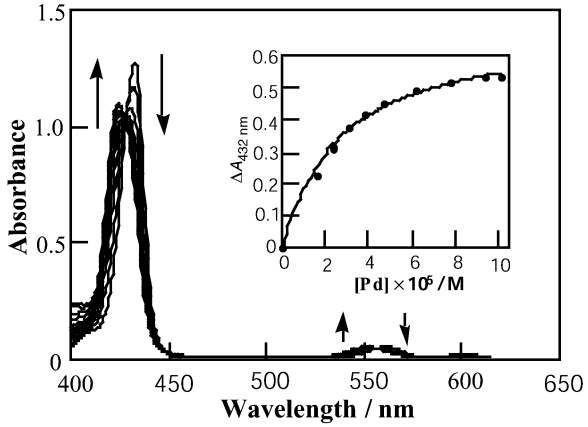

Fig. 2 Absorption spectral change of **1** (2.2 10^{-6} M) in toluene : CH_2Cl_2 = 50 : 1 (v/v) at 20 °C: [**2**] = 0–8.9 × 10^{-7} M, 1 cm cell. Inset: plot of ΔA_{432} *vs.* [**2**].

The UV–vis absorption spectra of **1** and the **1–2** complex[9] in the presence of C_{60} are shown in Fig. 3. It is seen from Fig. 3(a) that addition of C_{60} scarcely induces a spectroscopic change in the Soret band of **1**, indicating that the intramolecular pyridine–Zn(II) interaction is stronger than the intermolecular C_{60}–porphyrin interaction (*i.e.*, **1** is in the 'off' state). In contrast, the absorption spectrum of the **1–2** complex changed significantly upon addition of C_{60} (Fig. 3(b)), indicating that a significant interaction does exist between the **1–2** complex and C_{60} (*i.e.* the **1–2** complex is in the 'on' state: Scheme 1). From a plot of ΔA_{424} *vs.* [C_{60}] (insert in Fig. 3(b)), one can obtain $K = 5.1 \times 10^3$ M^{-1} for the formation of the 1 : 1 complex between C_{60} and the **1–2** complex.

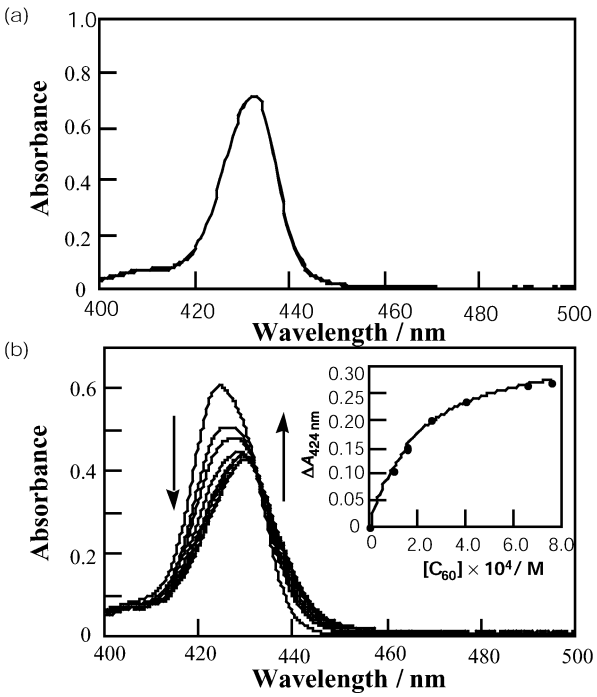

Fig. 3 Absorption spectral change of (a) **1** (1.1×10^{-5} M) and (b) **1** (1.1×10^{-5} M) and **2** (2.0×10^{-4} M) in toluene : CH_2Cl_2 = 50 : 1 (v/v) at 20 °C: [C_{60}] = 0–7.5×10^{-4} M, 1 mm cell. Inset: plot of ΔA_{424} *vs.* [C_{60}].

In conclusion, the present paper demonstrates that a novel bisporphyrin receptor **1**, which is efficiently interconverted between the *anti*- and the *syn*-conformation by interaction with the Pd(II) complex **2**, has been successfully designed. Since the **1–2** complex with *syn*-conformation has a large bisporphyrin-based cleft, it can accept C_{60} in the cavity. One can regard that this is a new example of positive, heterotropic allosterism.[10] Since we can control the ratio of the 'off' state and the 'on' state by the Pd(II) complex, this finding suggests a new strategy to control C_{60}-related chemical and physical functions. We believe that the present results will open a door to new inclusion chemistry toward switch-functionalized fullerene–porphyrin conjugates.

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Notes and references

† *Selected data* for **1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.99 (s, 8H), 8.86 (d, *J* 4.04 Hz, 4H), 8.68 (d, *J* 4.04 Hz, 4H), 8.28 (d, *J* 7.09 Hz, 4H), 8.18 (d, *J* 6.50 Hz, 2H), 8.13 (d, *J* 6.50 Hz, 2H), 8.08 (s, 2H), 8.03 (d, *J* 7.22 Hz, 4H), 7.64 (d, *J* 7.22 Hz, 4H), 7.60–7.54 (m, 8H), 8.86 (s, 2H), 6.20 (d, *J* 5.41 Hz, 4H), 4.55–4.52 (br, 4H), 4.38–4.36 (br, 4H), 3.95 (s, 6H), 2.74 (s, 12H), 2.72 (s, 6H), 2.55 (d, *J* 5.41 Hz, 4H); MALDI-TOF (Dithranol) *m/z* 1854.3 (M + H^+) (calc. 1854.5).

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