This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis and properties of fullerene (C_{70}) complexes of 2,6-bis(porphyrin)-substituted pyrazine derivatives bound to a Pd(II) ion

Yusaku Eda[a]; Kennosuke Itoh[a]; Yoshio N. Ito[a]; Mamoru Fujitsuka[b]; Tetsuro Majima[b]; Toshio Kawato[a]
[a] Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, Japan [b] The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Osaka, Japan

First published on: 09 June 2010

To cite this Article Eda, Yusaku , Itoh, Kennosuke , Ito, Yoshio N. , Fujitsuka, Mamoru , Majima, Tetsuro and Kawato, Toshio(2010) 'Synthesis and properties of fullerene (C_{70}) complexes of 2,6-bis(porphyrin)-substituted pyrazine derivatives bound to a Pd(II) ion', Supramolecular Chemistry, 22: 9, 517 — 523, First published on: 09 June 2010 (iFirst)

To link to this Article: DOI: 10.1080/10610278.2010.487566

URL: http://dx.doi.org/10.1080/10610278.2010.487566

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Supramolecular Chemistry
Vol. 22, No. 9, September 2010, 517–523

Synthesis and properties of fullerene (C_{70}) complexes of 2,6-bis(porphyrin)-substituted pyrazine derivatives bound to a Pd(II) ion

Yusaku Eda[a], Kennosuke Itoh[a], Yoshio N. Ito[a], Mamoru Fujitsuka[b], Tetsuro Majima[b] and Toshio Kawato[a]*

[a]*Department of Chemistry, Faculty of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan;*
[b]*The Institute of Scientific and Industrial Research (SANKEN), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

(*Received 12 November 2009; final version received 18 April 2010*)

2,6-Bis(porphyrin)-substituted 3,5-dimethylpyrazine and its zinc complex bound C_{70} to yield 1:1 inclusion complexes, which were characterised by ESI-MS, UV–vis, fluorescence and NMR spectroscopies. Association constants of the C_{70} complexes were determined by fluorescence and NMR spectral analyses. A decrease in absorbance of the Soret band of the pyrazine derivative by the effect of C_{70} was observed, suggesting the existence of a charge transfer interaction between C_{70} and porphyrin. Experimentally reliable values for the association constants were obtained by the NMR method and were about six times larger than those of the corresponding C_{60} complexes. Palladium complexation of the porphyrin–pyrazine ligand was found to enhance the association with fullerene. The association constant of 2,6-bis(porphyrin-Zn)-substituted 3,5-dimethylpyrazine-Pd(II) complex with C_{70} was determined to be $8400 \pm 900\,M^{-1}$. From the comparison of the association constants, it was found that inclusion room for C_{70} in the Pd(II) complex was maintained, juxtaposed between porphyrins attached to the opposite sides of the pyrazine ligands.

Keywords: fullerene; porphyrin; pyrazine; palladium(II) complex; association constant

Introduction

Once the significant properties of fullerene as an electron acceptor were recognised (*1*), many research attempts focused on the design and construction of host systems capable of capturing fullerene as a guest (*2–7*). In a previous paper, we reported the synthesis of 2,6-bis(porphyrin)-substituted pyrazine which bound C_{60} to form a 1:1 inclusion complex (*8*). Now we attempt to construct a supramolecular system by the aid of Pd(II) complexation with the pyrazine ligands. In order to develop a better understanding of such a fullerene-inclusion system, we have extended our investigation using C_{70} to show that the pyrazine ligand can embrace a proper fullerene between the porphyrins to form a stable inclusion complex. In this article, we will discuss structure and binding constants of a series of bis(porphyrin)-pyrazine derivatives with fullerenes.

Results and discussion

2,6-Bis(porphyrin)-substituted 3,5-dimethylpyrazine (**1**) and its Zn(II) complex (**2**) were prepared according to the previously reported procedure (*8*). Inclusion of C_{70} in the pyrazine ligand was confirmed first by means of mass spectrometry. The ESI-MS spectrum of a mixture of **1** and C_{70} exhibited a characteristic molecular ionic peak at 2022.4625 ($[\mathbf{1} + C_{70} + H]^+$), which provided evidence for the formation of a 1:1 complex of **1** and C_{70} (Figure 1). For the sake of comparing C_{70} with C_{60} as a guest for **1** and **2**, binding of C_{70} to **1** and **2** was then studied by the same methods as in the literature for C_{60} (*4*, *8*). The fluorescence spectrum of **1** in toluene (3.27 μM) exhibited a maximum at 650 nm upon excitation at 550 nm. The fluorescence due to porphyrin upon excitation at the Q-absorption band was diminished by the addition of C_{70} in toluene (Figure S1, available online). The Stern–Volmer plot for the fluorescence titration of **1** with C_{70} was found to be a straight line by plotting F_0/F vs. $[C_{70}]$, where F_0 and F are the fluorescence intensities at 650 nm of **1** without and with C_{70}, respectively (Figure S2, available online). From the line-fitting analysis, the association constant K_a was calculated to be $17550 \pm 170\,M^{-1}$. Analogous fluorescence quenching was observed for **2** with C_{70} in toluene (Figure S3, available online). However, the Stern–Volmer plot at 596 nm for the fluorescence titration of **2** with C_{70} was found to curve upward. Therefore, the association constant K_a for **2** and C_{70} was determined by the Benesi–Hildebrand equation at 596 nm to be $16400 \pm 600\,M^{-1}$. The binding isotherm provides a good fit to 1:1 stoichiometry (Figure S4, available online). These values for C_{70} are about 10 times larger than those of the corresponding C_{60} complexes (*8*). From these experiments, the association constants of C_{70} with **1** and **2** were determined to be larger than those of C_{60}. This result

---

*Corresponding author. Email: kawato@chem.kyushu-univ.jp

ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610278.2010.487566
http://www.informaworld.com

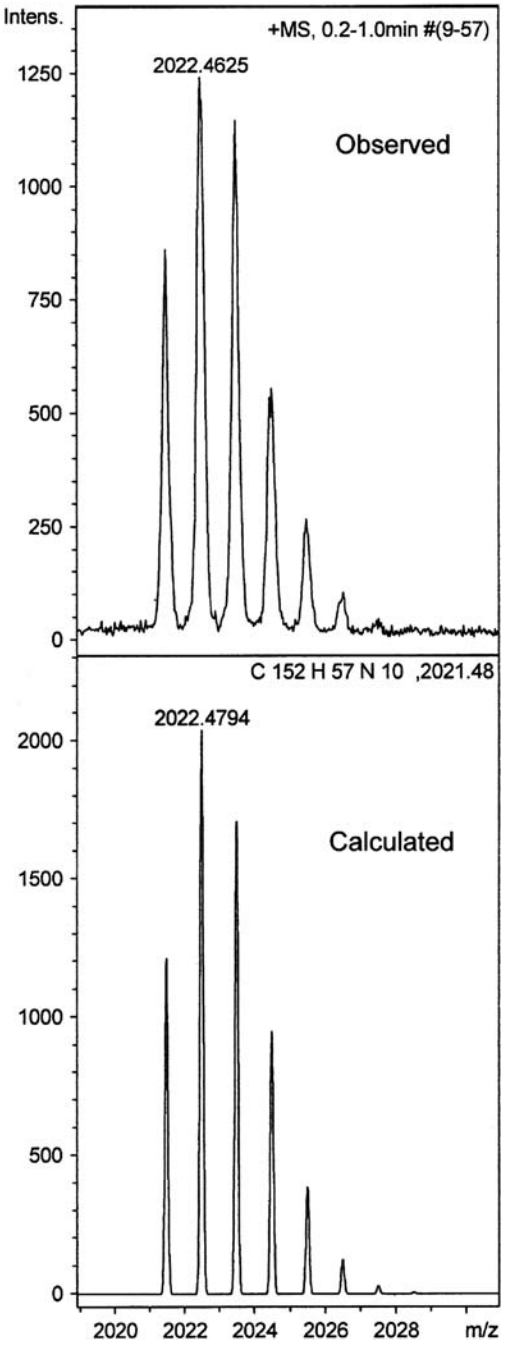


Figure 1. ESI-MS spectrum of a mixture of **1** and C_{70}.

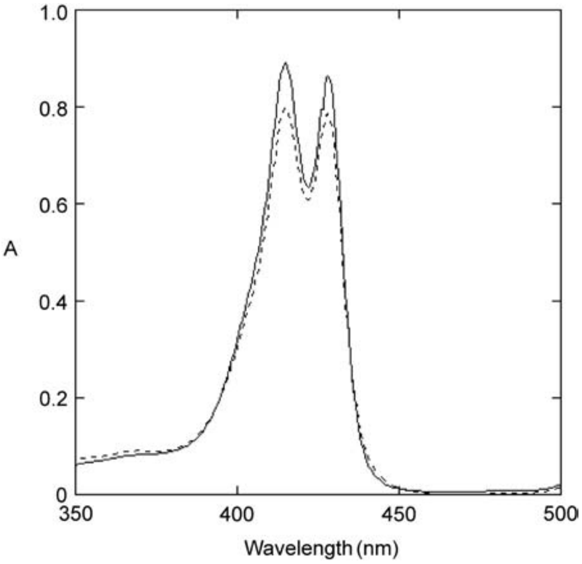
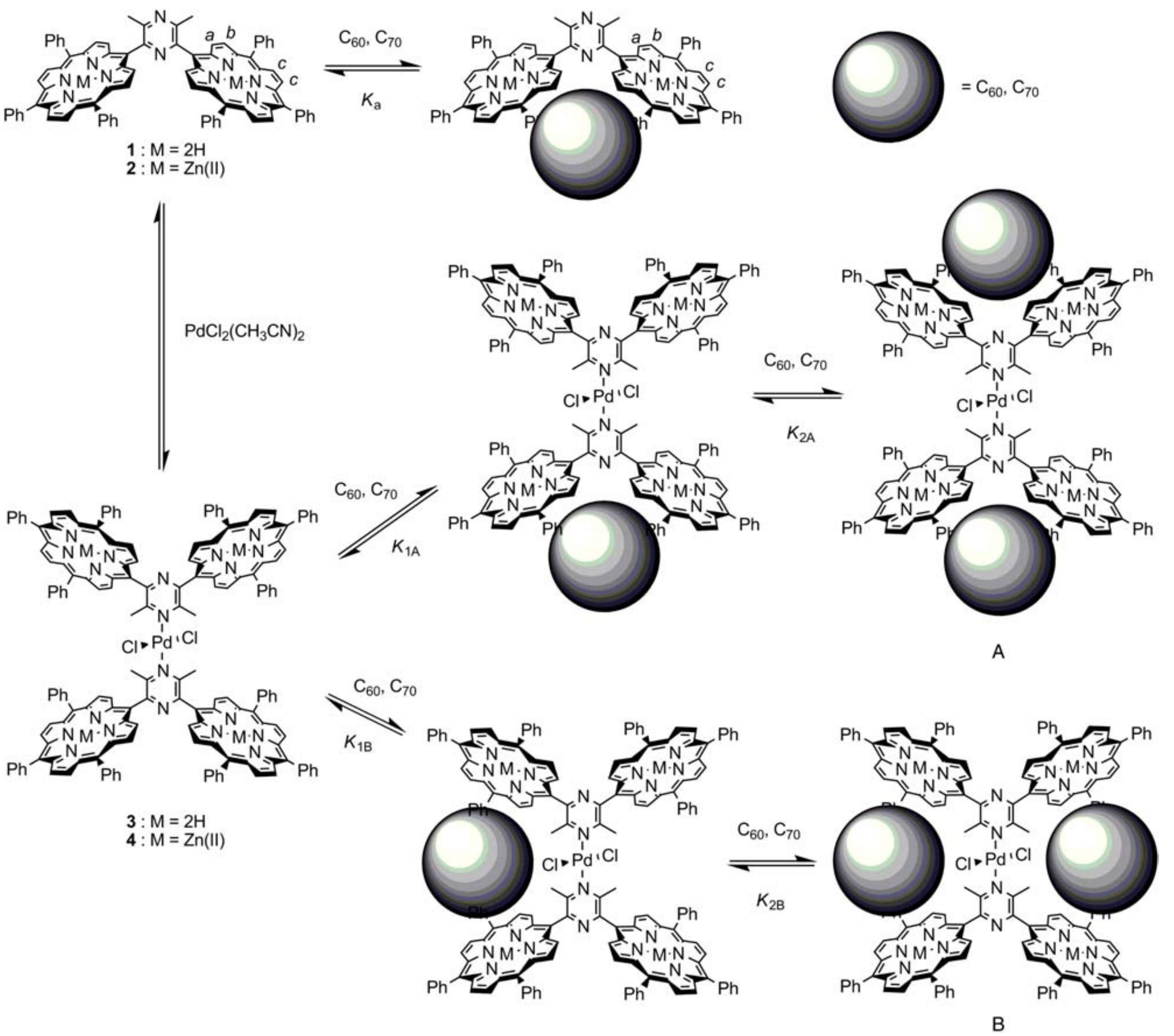


Figure 2. UV–vis absorption spectra of **1** (2.03 μM) before (solid line) and after (broken line) the addition of C_{70} (27.4 μM) in dichloromethane at 298 K (path = 1 cm).

shows that C_{70} fits well into the porphyrin–porphyrin pocket of **1** compared to C_{60}. Such a tendency is consistent with similar metalloporphyrins reported in the literature (*2*, *5*, *6*).

The UV–vis spectrum of **1** in dichloromethane was influenced by the addition of C_{70} (Figure 2). The decrease in absorbance of the Soret band of **1** by the effect of C_{70} suggests the existence of a charge transfer interaction between C_{70} and **1**. As the spectral change was too small to carry out a titration experiment to measure accurate binding data, the association constant of **1** and C_{70} was estimated to be 3530 M^{-1} from the difference of two absorbance measurements (0.0783 at 415 nm) taken of a solution of **1** (2.03 μM) before and after the addition of C_{70} (27.4 μM).

Association of **1** and C_{70} in solution was then investigated by a ^1H NMR titration method (270 MHz, 296 K, toluene-d_8). With increasing concentrations of C_{70} in a mixture of **1** and C_{70} in toluene-d_8, the β-pyrrole proton *a* near the pyrazine ring (Scheme 1) and NH proton of **1** shifted considerably upfield and the other β-pyrrole protons *b* and *c* shifted slightly upfield, whereas the protons of the methyl groups attached to the pyrazine ring shifted downfield (Figure 3). These experimental results were similar to the case of C_{60} (*5*–*7*). Thus, the complexation of C_{70} was considered to take place in the expected porphyrin–porphyrin pocket of **1** (Scheme 1). These shifts are larger than those caused by addition of C_{60}. NMR measurements of the methyl protons were suitable for the determination of the association constant K_a. The association constant K_a was determined to be 4800 ± 1300 M^{-1} by nonlinear curve fitting of the NMR data with K_a and δ_{max} treated as parameters (Figure 4). Complexation of **2** with C_{70} also takes place in solution as evidenced by changes in the chemical shifts of the protons of **2** by the addition of C_{70} (Figure 5). NMR measurements of the β-pyrrole proton *a* were suitable for the determination of association constant K_a. By a similar NMR titration method for **1**, the association constant K_a of **2** with C_{70} was determined to be 3400 ± 800 M^{-1} (Figure 6). The amount of the toluene solution of guest fullerene was more than that of the initial



Scheme 1. Possible structure of adducts of 2,6-bis(porphyrin)-substituted pyrazine derivatives (**1**–**4**) with fullerene.

host solution; however, we could not improve the NMR experimental conditions because of the low solubility of fullerene and its complex. Thus, the ^{1}H NMR titration method gave much smaller values for the association constant K_a than the fluorescence spectral method for **1** and **2**. In our previous paper (*8*), we reported that association constants obtained by fluorescence and the NMR titration method did not agree within estimated standard deviations. In this study, the value estimated by UV absorption spectra seemed to support the value measured by the NMR method. The error in the fluorescence method might originate in inaccurately detected fluorescence intensities which are attributed to the scattering of the incident beam by coexisting fullerene molecules in solution.

The association constant of C_{70} with Zn porphyrin complex **2** was smaller than that for **1** with metal-free porphyrins. This result is consistent with the result of calyx[4]arene-linked bis(porphyrin) hosts reported in the literature (*6*). Electron-rich porphyrin nitrogen atoms are effective for bond stabilisation by the dispersive forces associated with $\pi-\pi$ interactions between porphyrin and C_{70}.

Next, the metal complexation effect on the association of the pyrazine derivatives with fullerene was investigated. Complexation of **1** with Pd(II) ion was achieved by refluxing a solution of **1** and 1/2 molar amount of [$PdCl_2(CH_3CN)_2$] to afford **3** (Scheme 1). Comparison of the ^{1}H NMR peaks of **3** with those of **1** revealed a remarkable downfield shift ($\Delta\delta = 1.13$ ppm) for the

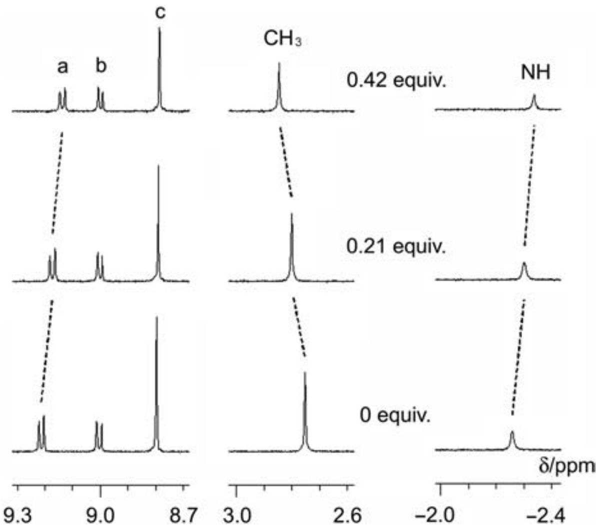


Figure 3. Partial ^{1}H NMR spectra (270 MHz, 296 K, toluene-d_8) of **1** with C_{70}. Assignments of peaks are shown in Scheme 1.

methyl peak upon complexation. Therefore, two pyrazine ligands coordinated to a Pd(II) ion at the nitrogen whose neighbouring carbons were connected to less hindered methyl groups. From the analogy of Pd(II) complexes with 2,6-disubstituted *N*-heterocyclic ligands (*8*, *9*), *cis*-coordination is impossible due to the steric repulsion between the substituents. Therefore, by the support of a Pd(II) ion to link two *trans*-pyrazine ligands, the juxtaposed porphyrin groups on the opposite side of the ligands can approach each other. Such an arrangement of the binding sites is essential for the system to work well as a host molecule (*9*).

The ground-state absorption spectrum of **3** displayed one broad Soret absorption peak at 418 nm (Figure 7). The figure is explained by the overlapping of peaks due to further splitting of the original Soret absorption bands by exciton couplings that originated from Coulombic interactions between transition dipole moments of the four porphyrins in **3**. The fluorescence spectrum of **3** exhibited a peak at 648 nm upon excitation by 553 nm light in dichloromethane (2.0 μM). As the emission from **3** is similar to that from free ligand **1** (emission peak maximum: 650 nm), the singlet excited state of **1** is not influenced by complexation with a Pd(II) ion. The UV–vis spectrum of **3** in dichloromethane was altered by the addition of C_{70} (Figure 7). The decrease in absorbance of the Soret band of **3** by the effect of C_{70} suggests the

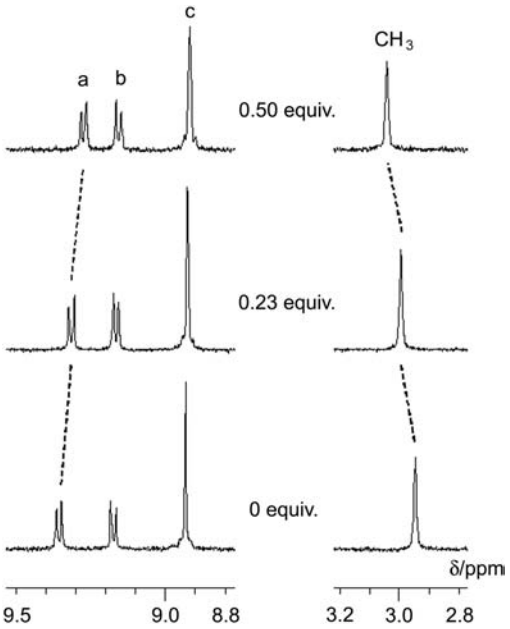


Figure 5. Partial ^{1}H NMR spectra (270 MHz, 296 K, toluene-d_8) of **2** with C_{70}. Assignments of peaks are shown in Scheme 1.

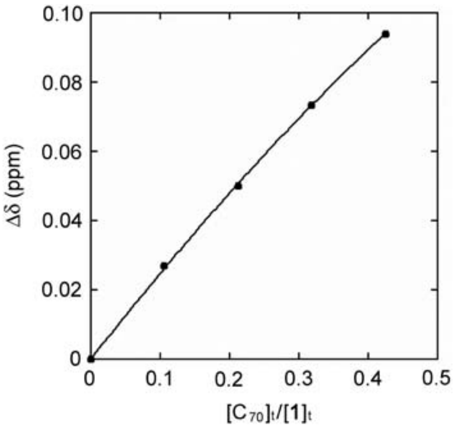


Figure 4. Changes in the chemical shift of the proton of the methyl group in **1** by the addition of C_{70} in toluene-d_8 at 296 K. The solid line is the theoretical isotherm obtained by nonlinear curve fitting to the experimental data.

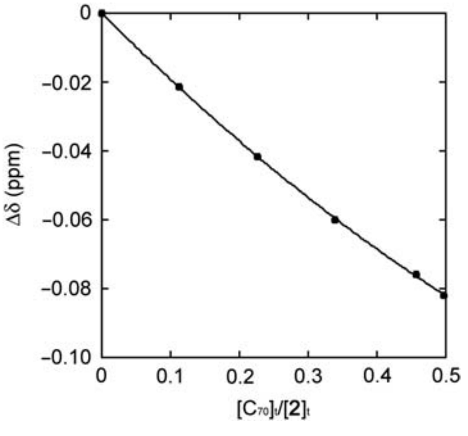


Figure 6. Changes in the chemical shift of β-pyrrole proton *a* in **2** by addition of C_{70} in toluene-d_8 at 296 K. The solid line is the theoretical isotherm obtained by nonlinear curve fitting to the experimental data.

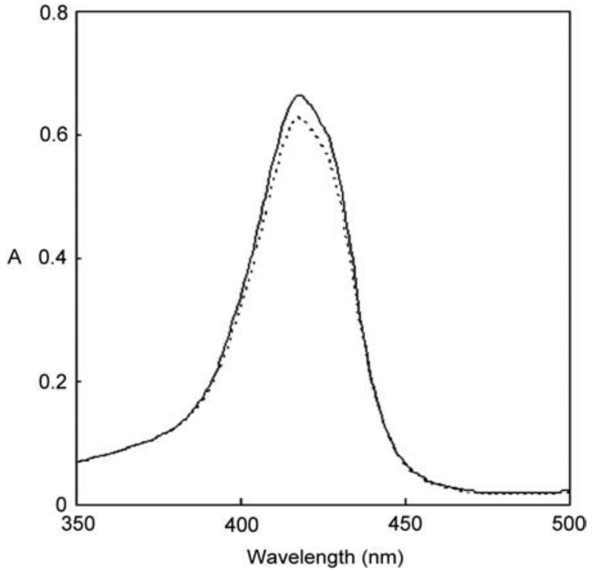


Figure 7. UV–vis absorption spectra of **3** (2.0 μM) before (solid line) and after (broken line) addition of C_{70} (27.5 μM) in dichloromethane at 298 K (path = 1 cm).

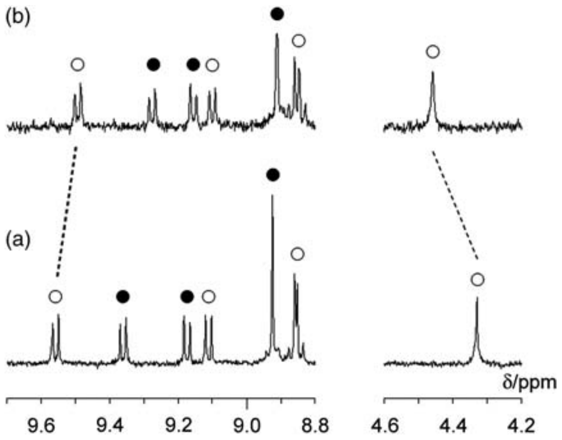


Figure 8. ^{1}H NMR spectra of 1:2 mixture of **4** (○) and **2** (●) before (a) and after (b) addition of an overall stoichiometric deficit of C_{70} in ratio 1:2:2.1.

existence of a charge transfer interaction between C_{70} and **3**. However, the degree of spectral change was not enough to measure an accurate binding constant for the complex. Furthermore, we could not carry out a ^{1}H NMR titration to measure the binding constant of **3** and C_{70} because of the low solubility of **3** in toluene. Thus, we could not determine the structure of the inclusion compound of **3** with C_{70}. Complexation of **2** with a Pd(II) ion was then achieved similarly by refluxing a solution of **2** and 1/2 molar amount of $[PdCl_2(CH_3CN)_2]$ to afford **4** (Scheme 1). As analytically pure Pd(II) complex was not obtained, the association of **4** and fullerene was investigated as a mixture of **2** and **4** by a ^{1}H NMR titration method (270 MHz, 296 K, toluene-d_8). With increasing concentrations of C_{70} in a mixture of **4** and C_{70} in toluene-d_8, the β-pyrrole proton *a* shifted considerably upfield and the other β-pyrrole protons shifted slightly upfield, whereas the protons of the methyl groups attached to the pyrazine ring shifted downfield (Figure 8). As probable structures of the complex of **4** and C_{70}, desired form **B** as well as form **A** was considered (Scheme 1). NMR data measurements of the β-pyrrole proton *a* were suitable for the determination of association constant K, which was found to be 7.1 $(\pm 1.5) \times 10^{7}\,M^{-2}$. The association constant K_1 was then calculated to be $8400 \pm 900\,M^{-1}$ because the value of K_2 would be equal to that of $K_1 (K = K_1 K_2 = K_1^2)$ due to the independence of the two sites of the host. This is attributed to no structural change of **4** after first binding with fullerene because the N—Pd—N bond is not likely to be flexible due to the steric hindrance of the methyl groups attached to the pyrazine rings. Possible forms of adducts of **4** and fullerene are shown in Scheme 1. In the case of form **A** in which inclusion room for C_{70} in the Pd(II) complex was maintained in the same position as that in **2**, the K_1 value should be close to the K_a of **2**. The fact that the value of K_1 is much larger than K_a of **2** suggests form **B** as the plausible structure of the adduct (*10*). Association of **4** and C_{60} in toluene-d_8 solution was similarly investigated. The association constant K was determined to be $4.3(\pm 0.8) \times 10^{6}\,M^{-2}$ and the association constant K_1 was estimated to be $2100 \pm 200\,M^{-1}$, which was 1/4 of that for C_{70}. Experimentally reliable association constants of bis(porphyrin)pyrazine derivatives and fullerene are summarised in Table 1. The effective enhancement of the binding with fullerene by Pd(II) complexation of the host is attributable to the proper bite angle (60° for **4** vs. 120° for **1** and **2**) formed by the two porphyrin rings to capture fullerene between them.

In conclusion, a pyrazine derivative with porphyrin rings at the 2,6-positions was a significantly better host for C_{70} than for C_{60}. The association constant of each adduct was determined successfully by an NMR titration method. It was found that palladium complexation of the porphyrin–pyrazine ligand enhanced the association of the host with fullerene. As photo-excited energy transfer is an important process in the early stages of photosynthesis (*11*), we are now attempting to construct a new system in

Table 1. Association constants of **1** and **2** (K_a/M^{-1}) and **4** (K_1/M^{-1}) with fullerene obtained by the ^{1}H NMR titration method (270 MHz, 296 K, toluene-d_8).

	C_{60}	C_{70}
1	830 ± 50 (*8*)	4800 ± 1300
2	550 ± 180 (*8*)	3400 ± 800
4	2100 ± 200	8400 ± 900

which photo-excited energy transfer arises from a proper metal ion to C_{70} through the bridging pyrazine moiety connecting the energy donor and acceptor.

Experimental section

General comments

UV–vis spectra were measured by a Shimadzu UV-2200 spectrophotometer. Fluorescence spectra were measured by a Hitachi F-2500 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GSX-270 FT NMR spectrometer with $CDCl_3$ or $C_6D_5CD_3$ as solvent and TMS as internal standard ($\delta = 0$ ppm). ESI-MS spectra were determined on a Bruker Daltonics MicroTOF-ks1focus ESI-TOF-MS spectrometer. Silica gel 60 (MERCK, Whitehouse Station, NJ, USA) was used for column chromatography. 2,6-Bis(10,15,20-triphenylporphyrin-5-yl)-3,5-dimethylpyrazine (**1**) and its Zn complex (**2**) were prepared according to the literature (*8*).

Materials

*trans-Dichlorobis[2,6-bis(10,15,20-triphenylporphyrin-5-yl)-3,5-dimethylpyrazine] palladium(II) (**3**)*

A solution of *trans*-$PdCl_2(CH_3CN)_2$ in benzene (1.7 mM, 0.933 ml) was added dropwise to a solution of **1** (3.8 mg, 3.2 μmol) in benzene (3 ml). After refluxing for 4 h, the solution was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2 to afford **3** (2.6 mg, 63%) as a purple solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ −2.79 (br s, 8H, NH), 3.77 (s, 12H, Pz-CH_3), 7.65–7.80 (m, 36H, PhH), 7.97–8.29 (m, 24H, PhH), 8.77 (s, 16H, β-pyrrole), 8.97–9.13 ppm (m, 16H, β-pyrrole); UV–vis (CH_2Cl_2): λ_{max} 418 ($\varepsilon = 330000$), 521 (36000), 553 (14000), 591 (9300), 646 nm (6300 $dm^3\,mol^{-1}\,cm^{-1}$); fluorescence (CH_2Cl_2, λ_{ex} 553 nm): λ_{em} 648 nm.

*trans-Dichlorobis[2,6-bis(zinc 10,15,20-triphenylporphyrin-5-yl)-3,5-dimethylpyrazine] palladium(II) (**4**)*

A solution of *trans*-$PdCl_2(CH_3CN)_2$ in benzene (1.7 mM, 0.332 ml) was added dropwise to a solution of **2** (1.5 mg, 1.1 μmol) in benzene (3 ml). After refluxing for 4 h, the solution was evaporated *in vacuo* to afford a mixture of **4** (50%) and starting material **2**, which was identified by NMR spectroscopy. The very limited solubility of the product and partial dissociation of the complex in solution precluded further purification. ^{1}H NMR (270 MHz, $C_6D_5CD_3$): δ 4.33 (s, 12H, Pz-CH_3), 7.42–7.61 (m, 36H, PhH), 8.03–8.28 (m, 24H, PhH), 8.85 (s, 8H, β-pyrrole), 8.86 (s, 8H, β-pyrrole), 9.11 (d, $J = 4.9$ Hz, 8H, β-pyrrole), 9.56 ppm (d, $J = 4.6$ Hz, 8H, β-pyrrole).

*^{1}H NMR titration experiment of **1** with C_{70} in toluene-d_8: general procedure*

A solution of **1** in toluene-d_8 (600 μl, 0.956 mM) was placed in an NMR sample tube and ^{1}H NMR spectra were recorded after each addition of 40, 80, 120 and 160 μl of a solution of C_{70} in toluene-d_8 (1.52 mM). The association constant K_a was evaluated from the change ($\Delta\delta$) in the chemical shifts of the β-pyrrole proton *a* of **1** by applying a nonlinear curve-fitting method using the equation shown below:

$$\Delta\delta = \Delta\delta_{max}([C_{70}]_t + [\mathbf{1}]_t + 1/K_a - (([C_{70}]_t + [\mathbf{1}]_t + 1/K_a)^2 - 4[C_{70}]_t[\mathbf{1}]_t)^{1/2})/(2[\mathbf{1}]_t),$$

where $[C_{70}]_t$ and $[\mathbf{1}]_t$ are total concentrations of C_{70} and **1**, respectively, and $\Delta\delta_{max}$ is $\Delta\delta$ at 100% complexation.

Supplementary material

Supplementary material (fluorescence titration data, full ESI-MS spectrum and full ^{1}H NMR spectra) associated with this article can be found online.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 20550125) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. We thank Prof. Tsutomu Katsuki and Dr Tatsuya Uchida of Kyushu University for their measurements of ESI-MS spectra.

References

(1) (a) Günes, S.; Neugebauer, H.; Sariciftci, N.S. *Chem. Rev.* **2007**, *107*, 1324–1338. (b) Gómez, R.; Seoane, C.; Segura, J.L. *Chem. Soc. Rev.* **2007**, *36*, 1305–1322. (c) Martín, N.; Sánchez, L.; Herranz, M.Á.; Illescas, B.; Guldi, D.M. *Acc. Chem. Res.* **2007**, *40*, 1015–1024. (d) Mateo-Alonso, A.; Guldi, D.M.; Paolucci, F.; Prato, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 8120–8126. (e) D'Souza, F.; Ito, O. *Coord. Chem. Rev.* **2005**, *249*, 1410–1422.

(2) (a) Tashiro, K.; Aida, T. *Chem. Soc. Rev.* **2007**, *36*, 189–197. (b) Boyd, P.D.W.; Reed, C.A. *Acc. Chem. Res.* **2005**, *38*, 235–242. (c) Wu, Z.-Q.; Shao, X.-B.; Li, C.; Hou, J.-L.; Wang, K.; Jiang, X.-K.; Li, Z.-T. *J. Am. Chem. Soc.* **2005**, *127*, 17460–17468.

(3) (a) Imahori, H. *J. Mater. Chem.* **2007**, *17*, 31–41. (b) Kuramochi, Y.; Satake, A.; Itou, M.; Ogawa, K.; Araki, Y.; Ito, O.; Kobuke, Y. *Chem. Eur. J.* **2008**, *14*, 2827–2841. (c) Trabolsi, A.; Urbani, M.; Delgado, J.L.; Ajamaa, F.; Elhabiri, M.; Solladié, N.; Nierengarten, J.-F.; Albrecht-Gary, A.-M. *New J. Chem.* **2008**, *32*, 159–165. (d) Hasobe, T.; Saito, K.; Kamat, P.V.; Troiani, V.; Qiu, H.; Solladié, N.; Kim, K.S.; Park, J.K.; Kim, D.; D'Souza, F.; Fukuzumi, S.J. *Mater. Chem.* **2007**, *17*, 4160–4170. (e) Tong, L.H.; Wietor, J.-L.; Clegg, W.; Raithby, P.R.; Pascu, S.I.; Sanders, J.K.M. *Chem. Eur. J.* **2008**, *14*, 3035–3044. (f) Sygula, A.; Fronczek, F.R.; Sygula, R.; Rabideau, P.W.; Olmstead, M.M. *J. Am. Chem. Soc.* **2007**, *129*, 3842–3843. (g) Pérez, E.M.; Sierra, M.; Sánchez, L.; Torres, M.R.; Viruela, R.;

Viruela, P.M.; Ortí, E.; Martín, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 1847–1851. (h) Nielsen, K.A.; Martín-Gomis, L.; Sarova, G.H.; Sanguinet, L.; Gross, D.E.; Fernández-Lázaro, F.; Stein P.C.; Levillain, E.; Sessler, J.L.; Guldi, D.M.; Sastre-Santos, Á.; Jeppesen, J.O. *Tetrahedron* **2008**, *64*, 8449–8463. (i) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250–5273. (j) Arimura, T.; Nishioka, T.; Suga, Y.; Murata, S.; Tachiya, M. *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 413–418. (k) Scheer, M.; Sachindler, A.; Merkle, R.; Johnson, B.P.; Linseis, M.; Winter, R.; Anson, C.E.; Virovets, A.V. *J. Am. Chem. Soc.* **2007**, *129*, 13386–13387.

(4) Bhattacharya, S.; Shimawaki, T.; Peng, X.; Ashokkumar, A.; Aonuma, S.; Kimura, T.; Komatsu, N. *Chem. Phys. Lett.* **2006**, *430*, 435–442.

(5) Dudič, M.; Lhoták, P.; Stibor, I.; Petříčková, H.; Lang, K. *New J. Chem.* **2004**, *28*, 85–90.

(6) Hosseini, A.; Taylor, S.; Accorsi, G.; Armaroli, N.; Reed, C.A.; Boyd, P.D.W. *J. Am. Chem. Soc.* **2006**, *128*, 15903–15913.

(7) Kubo, Y.; Sugasaki, A.; Ikeda, M.; Sugiyasu, K.; Sonoda, K.; Ikeda, A.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2002**, *4*, 925–928.

(8) Eda, Y.; Itoh, K.; Ito, Y.N.; Kawato, T. *Tetrahedron* **2009**, *65*, 282–288.

(9) (a) Mutou, T.; Amimoto, K.; Kanatomi, H.; Koyama, H.; Kawato, T. *Chem. Lett.* **1999**, 1231–1232. (b) Kawato, T.; Koyama, H.; Kanatomi, H.; Muramoto, Y. *Inorg. Chim. Acta* **1991**, *183*, 107–112.

(10) Sun, D.; Tham, F.S.; Reed, C.A.; Chaker, L.; Burgess, M.; Boyd, P.D.W. *J. Am. Chem. Soc.* **2000**, *122*, 10704–10705.

(11) (a) Stubbe, J.; Nocera, D.G.; Yee, C.S.; Chang, M.C.Y. *Chem. Rev.* **2003**, *103*, 2167–2202. (b) Pullerits, T.; Sundström, V. *Acc. Chem. Res.* **1996**, *29*, 381–389.