Tetrahedron 65 (2009) 282–288

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

2,6-Bis(porphyrin)-substituted pyrazine: a new class of supramolecular synthon binding to a transition-metal ion and fullerene (C_{60})

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ARTICLE INFO

Article history:
Received 4 September 2008
Received in revised form 17 October 2008
Accepted 18 October 2008
Available online 1 November 2008

Keywords:
Pyrazine
Porphyrin
Fullerene
Pd(II) complex

ABSTRACT

2,6-Disubstituted-3,5-dimethylpyrazines have been synthesized via biased acetal synthesis from symmetric 2,3,5,6-tetrakis(chloromethyl)pyrazine. The pyrazine ligands coordinated to *trans*-dichloropalladium(II) at the nitrogen whose neighboring carbons were connected to less hindered methyl groups. 2,6-Bis(porphyrin)-substituted pyrazine bound C_{60} to yield 1:1 inclusion complex. The binding of C_{60} with the pyrazine ligand and its zinc complex was determined by ESI-MS, NMR, and fluorescence spectroscopic analyses.

1. Introduction

There is much current interest in the supramolecular chemistry because of the remarkable applications in various fields of science and technology. Recently many research attempts have been centered on the design and construction of host systems that are capable of capturing fullerene C_{60} as a guest,[1–11] since its significant properties as electron acceptors were recognized.[12] Thus, many publications dealing with structural, spectroscopic, electrochemical, and other functional properties of supramolecular systems possessing C_{60} have appeared. Among them, disubstituted aromatic compounds could be arranged as good hosts by introducing certain functional groups for molecular recognition,[3–7] because two functional groups faced close to a guest.[13,14] As a consequence, 2,6-disubstituted pyridines were expected to be developed as unique host molecules.[14] On the other hand, due to the coordinative ability of aromatic nitrogen atoms, pyridine-based ligands have been widely used in the fields of metal coordination chemistry; thus, metal complexes of substituted pyridines have been developed.[15] In the case of pyrazine, two nitrogen atoms coordinate to different metal ions to act as *N*,*N*′-bidentate bridging ligands.[16] In such a polynuclear metal complex, metal ions can interact each other through the π-bonds of pyrazine ligands.

In view of the results, our interest in designing highly functional supramolecular systems has been directed toward the employment of a pyrazine derivative as a conjugated bridge that connects a functional metal ion and fullerene C_{60}. Although synthetic methods of substituted pyrazines have been developed in the fields of metal coordination chemistry as well as medicinal chemistry for the skeleton of biologically active sites,[17] considerable difficulty has been experienced in controlling circumstances around the two nitrogen atoms of pyrazine by introducing different type of substituents at the 2,6-positions and the 3,5-positions. In a previous paper, we have reported pyrazine acetal synthesis by a biased reaction of *trans*-bis(chloromethyl) substitutents of pyrazine with sodium alkoxides.[18] In this article, we have extended our investigation using the biased acetal synthesis from symmetric 2,3,5,6-tetrakis(chloromethyl)pyrazine (**1**) to provide a new type of pyrazine ligands with two functional groups that can be positioned to embrace C_{60} forming a 1:1 inclusion complex.

2. Results and discussion

Pivotal starting material, 2,6-bis(diethoxymethyl)-3,5-dimethylpyrazine (**2**), and its Pd(II) complex, *trans*-[$PdCl_2$(**2**)$_2$] (**3**), were prepared according to the previously reported procedure (Scheme 1).[18] In order to confirm the structures of the Pd complex **3** as well as the diacetal ligand **2**, X-ray crystallographic analysis of a single crystal of **3** was carried out in this study (Fig. 1). Two pyrazine ligands in **3** adopted C_2 symmetry and coordinated to a Pd(II) ion at the nitrogen whose neighboring carbons were connected to less hindered methyl groups. The N–Pd–Cl angles are 89.73(8)° and 90.27(8)° and the Pd–N and Pd–Cl bond lengths are 2.043(2) and 2.2916(11) Å,

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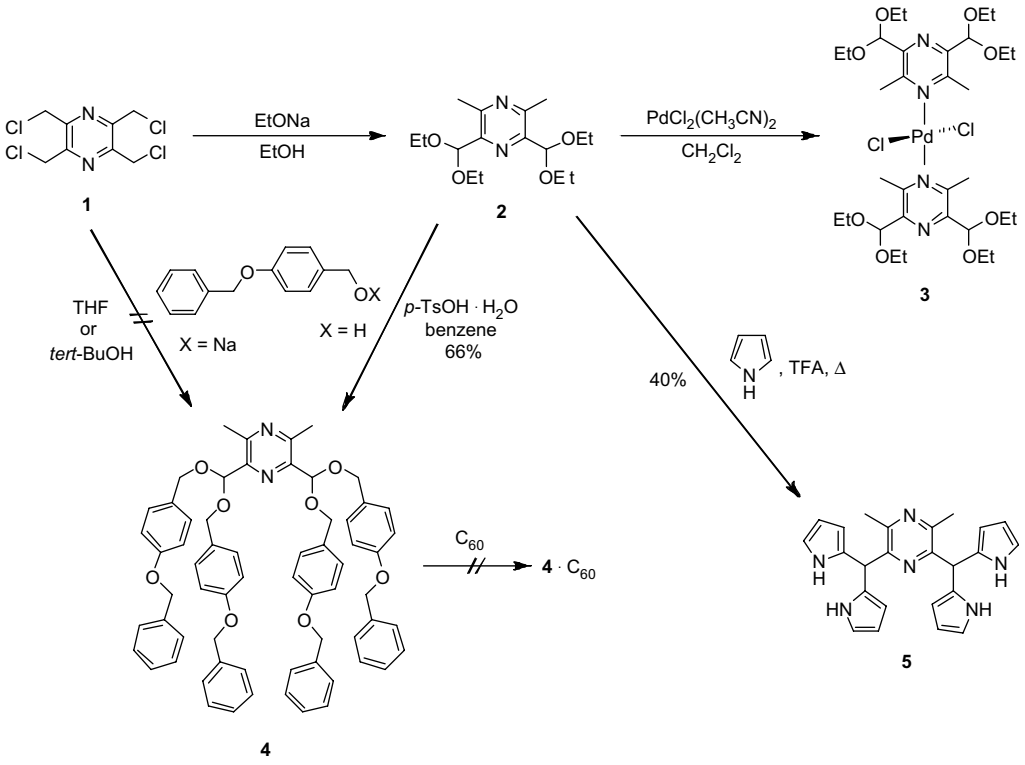
doi:10.1016/j.tet.2008.10.057



Scheme 1. Synthesis and reaction of bis(acetal)pyrazines (**2** and **4**).

respectively, falling in the normal range of those in common Pd(II) coordination compounds.[19]

Since metal complexation at one side of pyrazine nitrogen was achieved, inclusion of C_{60} at another side of the pyrazine ligand was attempted by introducing proper functional groups at 2,6-positions of pyrazine. We attended first to the work of Balch et al., who reported that electron-rich benzyl ether groups interacted with C_{60} to form supramolecular aggregation.[8] Thus, benzyloxybenzyl acetal compound **4** was chosen for the initial study largely for practical reasons; benzyloxybenzyl groups were considered to be easily introduced as pyrazine substituents by acetalization. Contrary to our previous result, however, reaction of **1** with sodium 4-benzyloxybenzyl alkoxide did not give intended benzyloxybenzyl acetal but yielded only intractable black material. The desired acetal **4** could be obtained by acid-catalyzed transacetalization of **2** with 4-benzyloxybenzyl alcohol as colorless glassy solid (Scheme 1). Such an acetal exchange reaction of **2** with slightly excess amount of other alcohols proceeded similarly to give corresponding pyrazine acetals; thus, compound **2** was found to be a convenient starting material for pyrazine derivatives. We then measured ^{1}H NMR of **4** before and after addition of C_{60} in toluene-d_8. Since their ^{1}H NMR spectra did not exhibit distinct difference in chemical shifts, association constant for **4** and C_{60} could not be determined by the ^{1}H NMR method. Although the possibility of encapsulation of C_{60} within **4** in solution cannot be rejected from the NMR data alone, low recognition ability of **4** with C_{60} is responsible for the high flexibility and low electronic interaction of benzyloxybenzyl group with C_{60}. This failure prompted introduction of more electron-donating and rigid substituents for functional groups.

Among supramolecular systems studied, porphyrin-based building blocks have been proved to be especially successful for holding C_{60}.[1,4–7,9–11] We thus examined covalent 2,6-difunctionalization of pyrazine with porphyrin to search C_{60} binding behavior (Scheme 2). For the synthesis of 2,6-bis(2,2′-dipyrromethyl)-3,5-dimethylpyrazine (**5**) as a precursor of porphyrin, diethyl acetal **2** was used without pre-hydrolysis to aldehyde because of synthetic convenience (Scheme 1), although dipyrromethane derivatives were generally prepared with aldehyde in pyrrole.[20] Acid-catalyzed condensation of **5** with 5-phenyldipyrromethane and benzaldehyde, followed by oxidation with DDQ, did not give desired

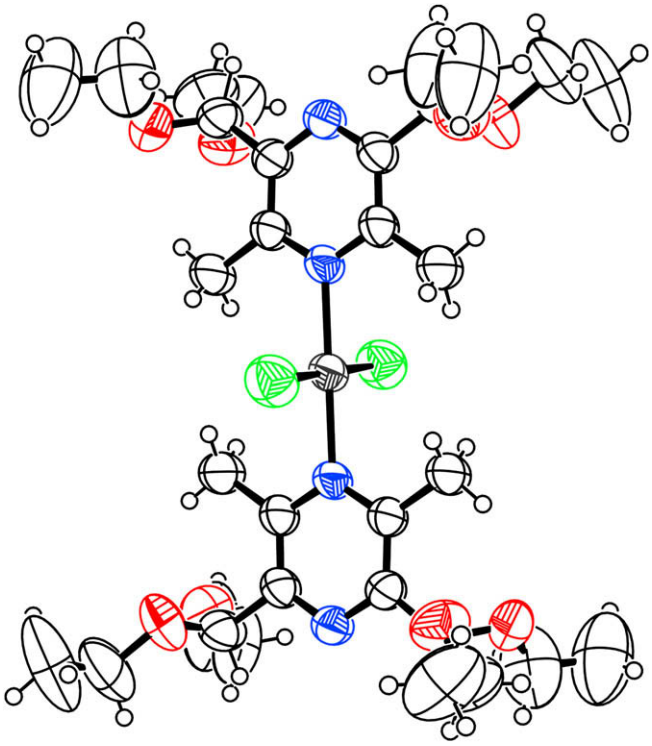
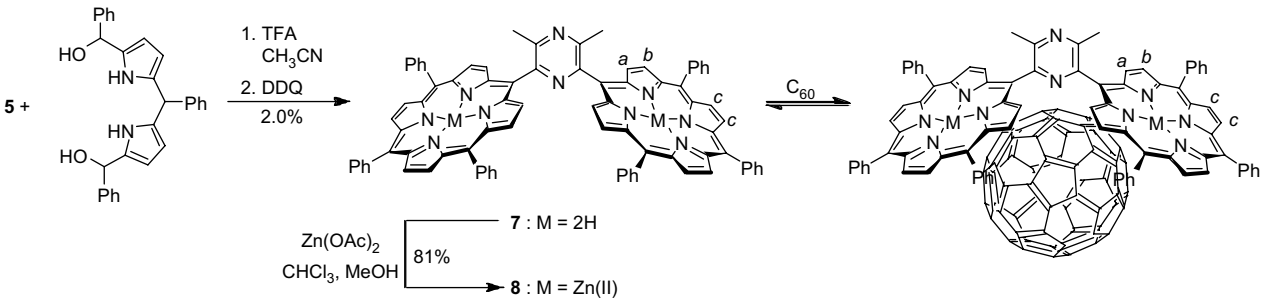


Figure 1. X-ray structure of Pd(II) complex **3**.



Scheme 2. Synthesis of bis(porphyrin)pyrazines (**7** and **8**) and their adducts with C_{60}.

porphyrin **7** but yielded polymer or polymer pigment. The preparation of porphyrins bearing one nitrogen heterocycle has been achieved successfully by bimolecular condensation of a dipyrromethane and a dipyrromethane-dicarbinol.[21] Therefore, dipyrromethane-dicarbinol **6** was prepared according to the literature and was employed for the synthesis of **7** (Scheme 2). Structure of the product **7** was determined by elemental analyses and ^{1}H NMR data. ESI-MS spectrum of a mixture of resultant **7** and C_{60} exhibited the molecular ionic peak due to the adduct at 1902.4938 ($[\mathbf{7}+C_{60}+H]^+$), which provided an evidence for the formation of a 1:1 complex of compound **7** and C_{60}. In order to confirm the coordination site of **7** to a Pd(II) ion, NMR spectra were measured after stepwise addition of $PdCl_2(CH_3CN)_2$ to **7** in $CDCl_3$. As a result, the downfield shift (from δ=2.64 to 3.67 ppm) for the peak due to the methyl groups attached to the pyrazine ring was observed, while the peak of the NH protons was intact, indicating that a Pd(II) ion was not inserted into the porphyrin ring. These observations suggested that **7** coordinated to a Pd(II) ion at the 4-nitrogen atom whose neighboring carbons were connected to less hindered methyl groups. For further study about the functionality of the porphyrin-substituents, we treated **7** with zinc acetate to yield porphyrin–zinc complex **8**.

Association of **7** and C_{60} in solution was first investigated by a ^{1}H NMR titration method (270 MHz, 296.5 K, toluene-d_8). With increasing concentrations of C_{60} in a mixture of **7** and C_{60} in toluene-d_8, β-pyrrole proton *a* near pyrazine ring (Scheme 2) and NH proton of **7** exhibited considerable upfield shifts and the other β-pyrrole protons *b*, *c* exhibited relatively small degree of upfield shifts (Fig. 2), while the protons of methyl groups attached to the pyrazine ring exhibited downfield shift. It is known that *meso*-aryl protons shift to a lower magnetic field, whereas β-pyrrole protons and pyrrole NH protons shift to higher magnetic fields as a result of interaction with C_{60}.[4,9] These experimental results show that β-pyrrole proton *a* is close to C_{60}, while the other pyrrole protons are far from C_{60}. Therefore, the complexation of C_{60} was considered to take place in the expected porphyrin–porphyrin cleft of **7** (Scheme 2). Such a conventional 1:1-type C_{60} binding was determined by Job's plot for change in ^{1}H NMR chemical shift due to β-pyrrole proton *a* by binding of C_{60} with **7** (Fig. 3). Measurement of NMR data due to the β-pyrrole proton *a* was also suitable for the determination of binding constant K_a, because the chemical shift change was largest in all β-pyrrole protons, thus, experimental error of the determined K_a was smallest for the experiment. The association constant K_a was determined to be $830\pm50\ M^{-1}$ by nonlinear curve-fitting of the NMR data with K_a and δ_{max} treated as parameters (Fig. 4). Moreover, in the ^{13}C NMR spectra, the signal of C_{60} shifted from 143.2 to 142.1 ppm due to the porphyrin ring current effect. This tendency in C_{60}- and porphyrin-induced chemical shift change in ^{13}C NMR spectra is consistent with those of recent reports on porphyrin–C_{60} systems.[4,5,10] Complexation of **8**

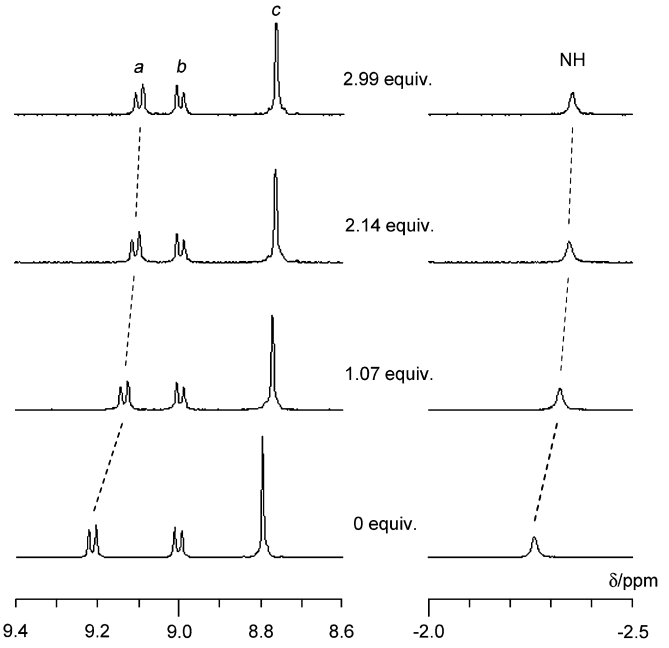


Figure 2. Partial ^{1}H NMR spectra (270 MHz, 296.5 K, toluene-d_8) of **7** with C_{60}. Assignments of peaks are shown in Scheme 2.

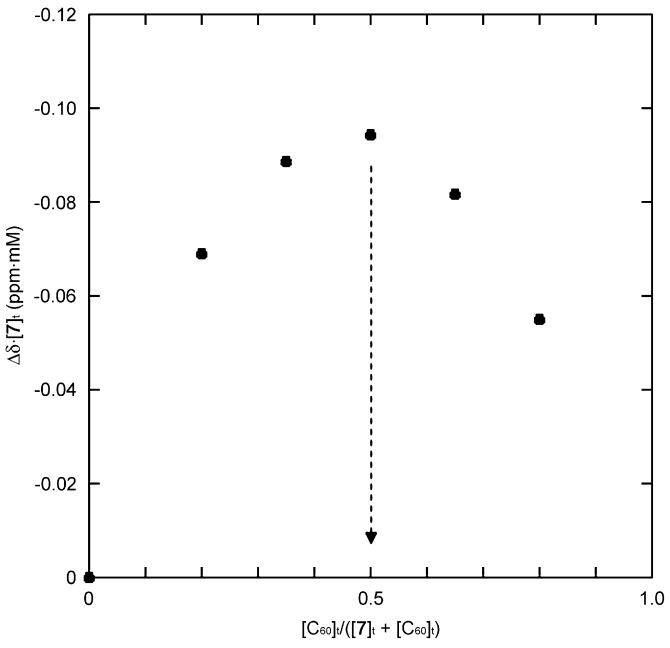


Figure 3. Job's plot for ^{1}H NMR chemical shift change of β-pyrrole proton *a* due to the binding of C_{60} with **7** (270 MHz, 296.5 K, toluene-d_8); $[\mathbf{7}]_t+[C_{60}]_t$=2.14 mM.

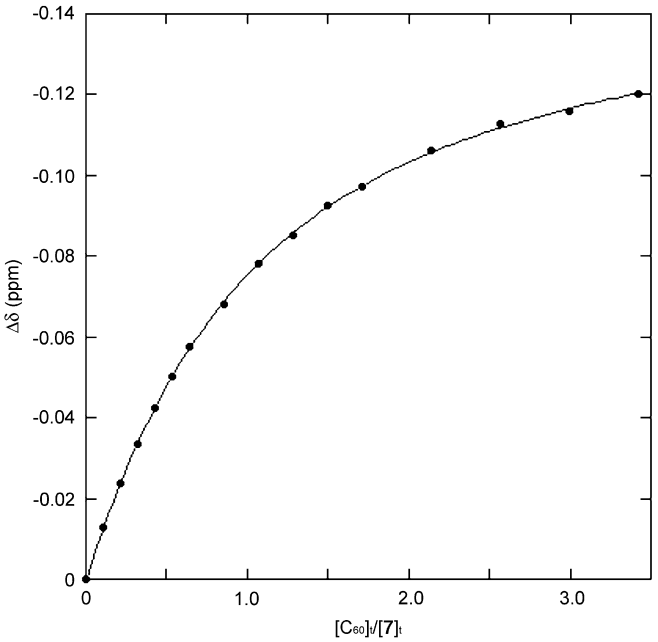


Figure 4. Change in the chemical shift of β-pyrrole proton *a* in **7** by addition of C_{60} in toluene-d_8 at 296.5 K. The solid line is the theoretical isotherm obtained by nonlinear curve-fitting to the experimental data.

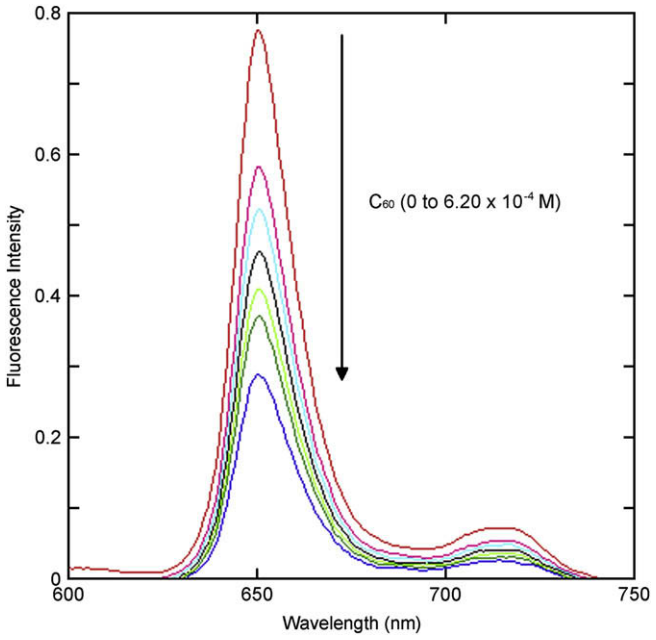


Figure 6. Fluorescence spectral changes for **7** (3.27 μM) by addition of C_{60} (0–6.20×10^{-4} M) in toluene at 298 K. Excitation wavelength=550 nm at the second Q-band of the UV–vis spectra.

with C_{60} also takes place in solution as evidenced by changes in the chemical shifts of the protons of **8** by addition of C_{60}. Such a chemical shift change for **8** was smaller than that of **7**. By a similar NMR titration method for **7**, the association constant K_a of **8** with C_{60} was determined to be 550±180 M^{-1}.

Ground state absorption spectrum of **7** displayed two split Soret absorption bands at 417 and 430 nm due to the presence of two porphyrin moieties (Fig. 5). Similar phenomenon of the splitting of Soret absorption band had been reported for an analogous bis(porphyrin)-aromatic compound, in which 3,5-dimethylpyrazine ring of **7** was replaced by a phenyl ring (1,3-bis(10,20-diundecyl-21*H*,23*H*-porphyrin-5-yl)benzene: **DP**).[6] As for the Q-absorption bands, **7** showed one major absorbance at 516 nm and three minor bands at 550, 591, and 648 nm. Zinc complex **8** also exhibited two split Soret absorption bands at 420 and 434 nm, but small red shifts and decrease of the intensity of both bands were observed (Fig. 5). Little changes in UV–vis spectra for **7** and **8** by addition of C_{60} were observed. These results suggest that there is little charge transfer interaction between C_{60} and **7** or **8**.

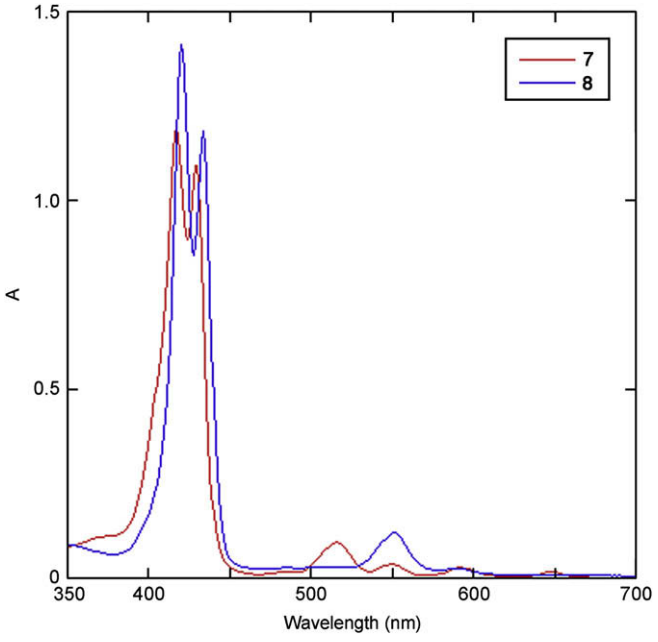


Figure 5. UV–vis absorption spectra of **7** (2.62 μM) and **8** (4.51 μM) in toluene at 298 K.

Binding of C_{60} with **7** and **8** was then determined by fluorescence spectroscopy. The fluorescence spectra of **7** in toluene (3.27 μM) exhibited maxima at 650 nm upon excitation at 550 nm. It was found that the fluorescence of porphyrin upon excitation at Q-absorption band diminished with C_{60} in toluene (Fig. 6). Stern–Volmer plot for the fluorescence titration of **7** with C_{60} was found to curve upward (Fig. 7). Such a nonlinear curvature suggests that the excited state of porphyrin in **7** is quenched in both static and dynamic processes. In other words, the fluorescence of **7** in the complex is interpreted as a result of partial quench by an intra-ensemble electron transfer process involving a complexed C_{60}.[11] Therefore, the association constant K_a for **7** and C_{60} was determined by the use of Benesi-Hildebrand equation. A straight line was obtained by plotting $F_0/(F_0-F)$ versus $1/[C_{60}]$, where F_0 and F are the fluorescence intensity at 650 nm of **7** without and with C_{60}, respectively, indicating the 1:1 stoichiometry of the complex of **7** and C_{60} (Fig. 8). The association constant K_a was calculated from ratio for the intercept versus slope to be 1680±120 M^{-1}. This value was broadly in agreement with that of its phenyl analogue **DP**,[6] 1975±105 M^{-1}, which was determined by Stern–Volmer method.

Analogous fluorescence quenching was observed for **8** with C_{60} in toluene (Fig. 9). Since Stern–Volmer plot at 596 nm for **8** was curved upward as in the case of **7**, the association constant K_a for **8** and C_{60} was determined similarly by the Benesi–Hildebrand equation to be 1500±120 M^{-1}.

The association constant of C_{60} with Zn–porphyrin complex **8** shows decreased binding energies relative to uncomplexed porphyrin of **7**. This result is consistent with the propensity in metallo-porphyrins reported in the literature.[7,10] The electron-rich porphyrin nitrogen atoms are effective for the bond-stabilization by

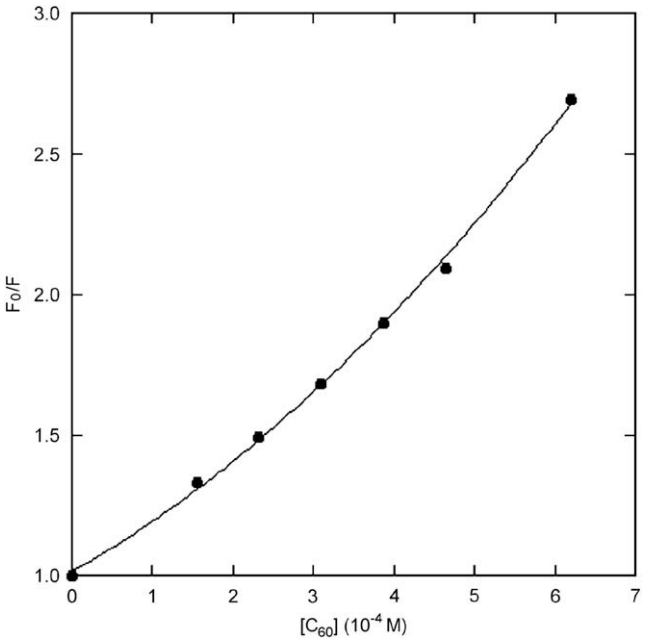


Figure 7. Stern–Volmer plot for the fluorescence quenching at 650 nm of **7** with C_{60} in toluene.

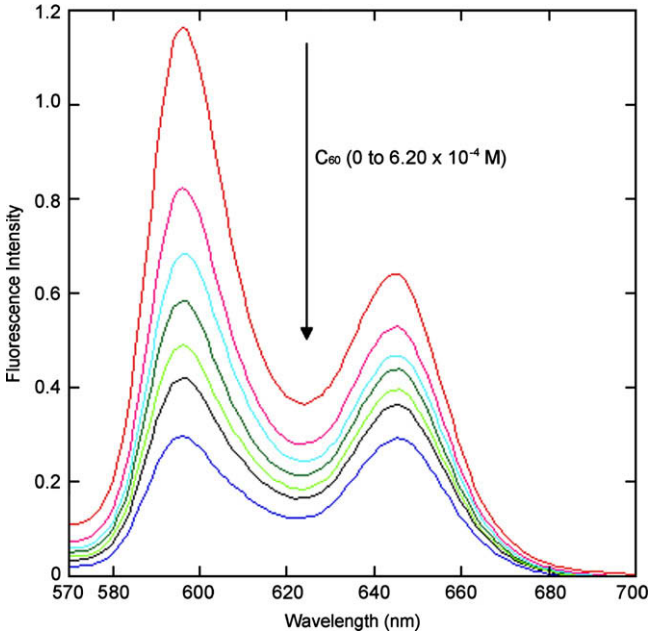


Figure 9. Fluorescence spectral changes of **8** (2.26 μM) by addition of C_{60} (0–6.20×10^{-4} M) in toluene at 298 K. Excitation wavelength=551 nm at the first Q-band of the UV–vis spectra.

the dispersive forces associated with π–π interactions between porphyrin and C_{60}. The ^{1}H NMR titration method offered much smaller values for the association constant K_a than the fluorescence spectral titration for **7** and **8**. Since the binding constants obtained by two different methods do not agree within the Estimated Standard Deviations (ESD), the two methods may be measuring different reactions occurred under different concentrations of the host and C_{60}. The discrepancies may be related to the changes in the fluorescence shown in Figure 9. The relative intensity of the two bands at 596 and 645 nm changes during the titration, though exact reason is not clear as things stand now. Because of the low solubility of C_{60} and its complex in toluene, we could not improve the experimental conditions of NMR titration, in which the amount of the toluene solution of guest C_{60} was too much for that of the initial host solution. As a result, low values by NMR titration method might not exhibit correct K_a values. The K_a value of **7** by fluorescence spectral method is slightly smaller than the value for **DP**.[6] The difference in the K_a values is ascribed to the distinction of experimental methods rather than the negative effect of pyrazine nitrogen. This feature encourages the use of bis(porphyrin)pyrazine as a synthon of functional supramolecular systems with metal ions.

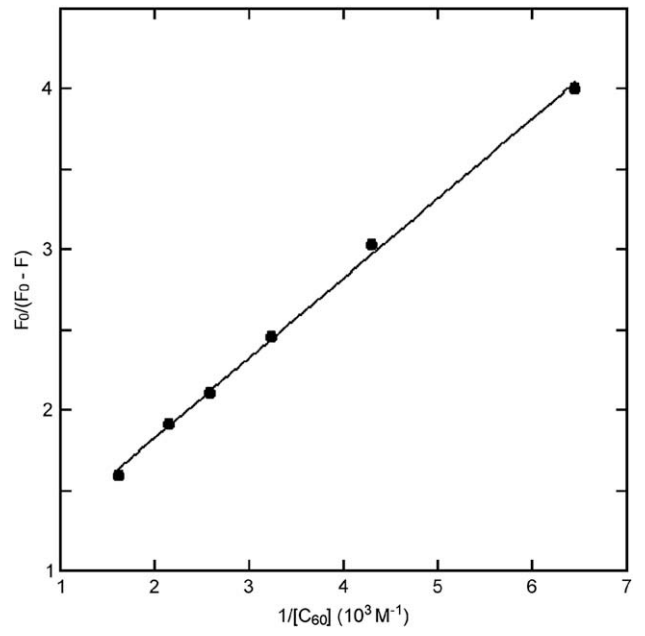


Figure 8. Benesi–Hildebrand plot for the quenching at 650 nm of **7** with C_{60} in toluene.

3. Conclusion

In this study, pyrazine derivatives could be arranged as a good host for C_{60} by introducing porphyrin rings at the 2,6-positions. On the other hand, 3,5-dimethylpyrazine-2,6-diacetal was found to coordinate Pd(II) ion at 4-nitrogen whose neighboring carbons were connected to less hindered methyl groups. Accordingly, circumstances around the two nitrogens of pyrazine were controlled by the introduction of proper substituents at proper positions. From these results, starting 2,6-pyrazine diacetals have been proved to be versatile in the synthesis of highly functionalized ligands. Such disproportioned pyrazines should presage interesting supramolecular systems.

4. Experimental

4.1. General comments

All melting points (mp) were measured by a YAMATO model MP-21 melting point apparatus or a Yanaco model MP-500V micro melting point apparatus and were uncorrected. UV–vis spectra were measured by a SHIMADZU UV-2200 spectrophotometer. Fluorescence spectra were measured by a HITACHI F-2500 spectrophotometer. ^{1}H and ^{13}C 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 (δ=0 ppm). Pyrazine ring is written in the abbreviation Pz for the peak assignment. ESI-MS spectra were determined on a Bruker Daltonics MicroTOF-ks1focus ESI-TOF-MS spectrometer. Elemental analyses were performed by the Service

Center of the Elementary Analysis of Organic Compounds affiliated to the Faculty of Sciences in Kyushu University. Silica gel (MERCK, Silica gel 60) and alumina (MERCK, Aluminum oxide 90 active neutral) were used for column chromatography. Silica gel (Wako, Wakogel FC-40) was used for flash column chromatography and medium pressure liquid column chromatography. Benzene and pyrrole were freshly distilled at atmospheric pressure prior to use. DDQ was recrystallized from chloroform. All other reagents were obtained from commercial suppliers and used without further purification. 2,6-Bis(diethoxymethyl)-3,5-dimethylpyrazine (**2**),[18] *trans*-dichlorobis[2,6-bis(diethoxymethyl)-3,5-dimethylpyrazine] palladium(II) (**3**),[18] and dipyrromethane-dicarbinol **6**[21] were prepared according to the literature.

4.2. Materials

*4.2.1. 2,6-Bis[di(4-benzyloxybenzyloxy)methyl]-3,5-dimethylpyrazine (**4**)*

A mixture of **2** (318 mg, 1.0 mmol), 4-benzyloxybenzyl alcohol (946 mg, 4.4 mmol), and *p*-toluenesulfonic acid monohydrate (9 mg, 0.05 mmol) in benzene (40 ml) was refluxed for 18 h, during which period resultant ethanol was removed by a Dean–Stark trap with molecular sieve MS 5 Å. The resulting mixture was neutralized with triethylamine and the solvent was removed by evaporation. The yellow residue was purified by medium pressure liquid column chromatography on silica gel, eluting with ethyl acetate–*n*-hexane mixture (1:4 v/v) to afford **4** (663 mg, 66%) as a colorless glassy solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ=2.62 (s, 6H, Pz–CH_3), 4.51 (d, J=11.5 Hz, 4H, OCH_2–Ph–), 4.66 (d, J=11.5 Hz, 4H, OCH_2–Ph–), 5.01 (s, 8H, Ph–CH_2O–), 5.63 (s, 2H, Pz–CH), 6.87–6.99 (m, 8H, PhH), 7.20–7.42 ppm (m, 28H, PhH); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ=158.5, 151.8, 146.1, 136.9, 129.9, 129.6, 128.6, 127.9, 127.4, 114.7, 102.7, 70.0, 69.1, 21.0 ppm. Anal. Calcd for $C_{64}H_{60}N_2O_8$: C, 78.03; H, 6.14; N, 2.84%. Found: C, 77.89; H, 6.18; N, 2.68%.

*4.2.2. 2,6-Bis(2,2′-dipyrromethyl)-3,5-dimethylpyrazine (**5**)*

A mixture of **2** (1.25 g, 4.0 mmol) and pyrrole (7.13 ml) was degassed with bubbling of nitrogen for 10 min. TFA (30 μl) was injected and the solution was stirred at 50 °C for 3 h until the starting aldehyde disappeared. The solution was then diluted with 36 ml of chloroform and was washed with 0.1 M NaOH aq (1×8 ml, 1×10 ml, 1×12 ml) and water (3×12 ml). The organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was distilled under reduced pressure to remove remaining pyrrole. The residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate–*n*-hexane–triethylamine mixture (50:50:1 v/v), followed by crystallization from ethanol to afford **5** (639 mg, 40%) as light brown needles. Mp 180.2–181.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ=2.62 (s, 6H, Pz–CH_3), 5.66 (s, 2H, *meso*-H), 5.86–5.88 (m, 4H), 6.12 (q, J=2.2 Hz, 4H), 6.58–6.63 (m, 4H), 8.22 ppm (br s, 4H, NH). Anal. Calcd for $C_{64}H_{60}N_2O_8$: C, 72.70; H, 6.10; N, 21.20%. Found: C, 72.68; H, 6.13; N, 21.13%.

*4.2.3. 2,6-Bis(10,15,20-triphenylporphyrin-5-yl)-3,5-dimethylpyrazine (**7**)*

To a mixture of **5** (142 mg, 0.36 mmol) and the dipyrromethane-dicarbinol **6** (0.72 mmol) in acetonitrile (280 ml) was added TFA (0.63 ml, 8.5 mmol) under protection from light. After 10 min, DDQ (483 mg, 2.1 mmol) was added to the solution, which was stirred for 1 h at room temperature. After addition of triethylamine (1.17 ml, 8.4 mmol), the entire reaction mixture was filtered through a pad of alumina (3×10 cm) and eluted with CH_2Cl_2 until the elutant was no longer dark. The resulting porphyrin solution was concentrated in vacuo and the residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2 and then CH_2Cl_2–ethyl acetate mixture (99:1 v/v), followed by recrystallization from CH_2Cl_2–methanol to afford **7** (8.20 mg, 2.0%) as a purple solid. Mp >300 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ=−2.71 (br s, 4H, NH), 2.64 (s, 6H, Pz–CH_3), 7.70–7.81 (m, 18H, PhH), 8.07–8.21 (m, 8H, PhH), 8.30–8.31 (m, 4H, PhH), 8.82 (s, 8H, β-pyrrole), 9.00 (d, J=4.9 Hz, 4H, β-pyrrole), 9.12 ppm (d, J=4.9 Hz, 4H, β-pyrrole); UV–vis (toluene): λ_{max}=417 (ε=454,000), 430 (416,000), 516 (36,200), 550 (14,300), 591 (10,600), 648 nm (6670 dm^3 mol^{-1} cm^{-1}); ESI-MS obsd 1181.4754, calcd 1181.4762 ([M+H]$^+$, M=$C_{82}H_{56}N_{10}$). Anal. Calcd for $C_{82}H_{56}N_{10}\cdot 1/2H_2O$: C, 82.74; H, 4.83; N, 11.77%. Found: C, 82.55; H, 4.70; N, 11.78%.

*4.2.4. Zn(II) complex of 2,6-bis(10,15,20-triphenylporphyrin-5-yl)-3,5-dimethylpyrazine (**8**)*

A saturated solution of zinc acetate in methanol (0.1 ml) was added to a solution of **7** (3.90 mg, 3.3 μmol) in chloroform (4 ml) and the mixture was stirred overnight at room temperature. The solvent was removed by evaporation and the residue was dissolved in chloroform (4 ml). The solution was washed with water (3×4 ml) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo to afford **8** (3.50 mg, 81%) as a purple solid. ^{1}H NMR (270 MHz, $C_6D_5CD_3$): δ=2.94 (s, 6H, Pz–CH_3), 7.45–7.59 (m, 18H, PhH), 8.09–8.28 (m, 12H, PhH), 8.92 (s, 8H, β-pyrrole), 9.17 (d, J=4.6 Hz, 4H, β-pyrrole), 9.36 ppm (d, J=4.9 Hz, 4H, β-pyrrole); UV–vis (toluene): λ_{max}=420 (ε=313,000), 434 (262,000), 551 (26,800), 590 nm (5990 dm^3 mol^{-1} cm^{-1}).

4.3. X-ray crystallography of Pd(II) complex 3

A single crystal suitable for X-ray diffraction was obtained by recrystallization from a mixture of dichloromethane and *n*-hexane. The crystal was mounted at the end of a glass fiber. X-ray diffraction experiments were performed at 293 K on a Rigaku RAXIS RAPID X-ray diffractometer with graphite monochromated Mo Kα radiation (λ=0.71075 Å) and a rotating anode generator. Absorption corrections were applied (absorption coefficient μ=0.617 mm^{-1}) to the raw intensity data. Of the 10,166 reflections, which were collected, 4736 were independent (R_{int}=0.027); equivalent reflections were merged. Data analysis was carried out with the Crystalstructure™ crystallographic software package. The structure was solved by direct methods using SIR92 and refined by a full matrix least-squares procedure on F^2 with SHELXL-97. The refinement converged at $R1$=0.046, $wR2$=0.122, with $I>2.0\sigma(I)$. The structure of molecule was obtained by ORTEP3 included in the Crystalstructure™ software.

Crystal data. $C_{32}H_{56}Cl_2N_4O_8Pd$, M=802.11, triclinic, space group P-1 (#2), a=7.6227(8) Å, b=11.4031(9) Å, c=12.0607(10) Å, α=92.648(2)°, β=90.933(4)°, γ=91.881(4)°, V=1046.49(16) Å^3, Z=1, calculated density D_{calcd}=1.273 g cm^{-3}, crystal size 0.25×0.25×0.2 mm.

Full crystallographic data for the structure of **3** in this paper have been deposited with the Cambridge Crystallographic Data Centre under deposition number 691723. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.4. ^{1}H NMR titration experiment of 7 with C_{60} in toluene-d_8: general procedure

A solution of **7** in toluene-d_8 (600 μl, 1.34 mM) was taken in an NMR sample tube and ^{1}H NMR spectrum was recorded after each addition of 40, 80, 120, 160, 200, 240, 320, 400, 480, 560, 640, 800, 960, 1120, and 1280 μl of a solution of C_{60} in toluene-d_8 (2.14 mM). Association constant K_a was evaluated from the change ($\Delta\delta$) in the chemical shifts of the β-pyrrole proton *a* of **7** applying a nonlinear curve-fitting method using the equation shown below:

$$\Delta\delta = \Delta\delta_{max}([C_{60}]_t + [\mathbf{7}]_t + 1/K_a - (([C_{60}]_t + [\mathbf{7}]_t + 1/K_a)^2 - 4[C_{60}]_t \times [\mathbf{7}]_t)^{1/2})/(2[\mathbf{7}]_t)$$

where $[C_{60}]_t$ and $[\mathbf{7}]_t$ are total concentrations of C_{60} and **7**, respectively; $\Delta\delta_{max}$ is $\Delta\delta$ at 100% complexation.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research (No. 20550125 and No. 17029049 on Priority Areas (417)) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. We thank Professor Tsutomu Katsuki of Kyushu University for his kind support throughout the measurement of ESI-MS spectra and X-ray crystallography. We also thank Dr. Kiichi Amimoto of Hiroshima University for his advices and stimulating discussion for X-ray analysis.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.057.

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