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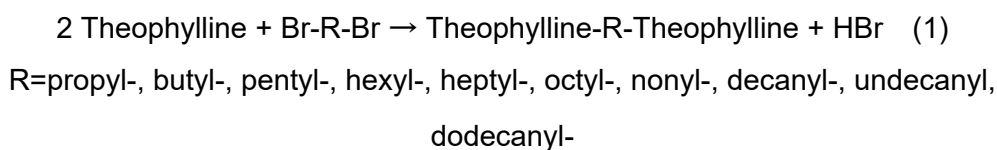
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1. Experimental Procedures

1-1. Synthesis of theophylline ligand

Ligand molecules containing theophylline as a chelate agent used in this study were prepared modifying literature procedure.[1] The *bis*-theophylline alkane were synthesized from the reaction between theophylline and alkyl-dibromide in the presence of potassium carbonate in methanol at 70 °C according to the following reaction(Eq. (1)).



Typical example of synthesis of bisditheophyllineheptan(BTC₇) was described as follows. To a 300 mL eggplant type flask equipped with a condenser, methanol (solvent, 200 mL), K₂CO₃ (base, 3.46 g, 25 mmol), and theophylline (3.96 g, 22 mmol) were added, and the mixture was stirred at 70 °C until solution became clear. Then, dibromoheptane (C7: 2.63 g, 10 mmol) was added and the mixture was refluxed at 80 °C for 96 h. After that, the reaction mixture was evaporated to remove methanol. Then the product was extracted from chloroform/water. After concentration the chloroform solution, the product (BTC₇) was recrystallized in ethyl acetate by which white powders were obtained.

1-2. Preparation of nanostructured palladium-theophylline flowers by complexation-driven self-assembly

Complexation of BTC₇ and palladium (II) chloride was performed from a water-ethanol mixture. The ethanol solution of BTC₇ (5.0 mmol dm⁻³) was prepared by dissolving 570 mg of BTC₇ into 250 mL of analytical grade ethanol. The aqueous solution of PdCl₂ (5.0 mmol dm⁻³) was prepared by dissolving palladium (II) chloride in 1.0 M hydrochloric acid. Then, equal volumes (250 mL) of both same concentration solutions were mixed and left 1 month. Yellow precipitates (PdBTC₇) formed spontaneously were filtrated and washed by water and ethanol alternatively, and dried at ambient condition.

1-3. Suzuki-Miyaura cross-coupling reactions

In a typical reaction, 0.317 mg of PdBTC₇ (MW=633.83) (this equates to 0.1 mol% Pd relative to bromobenzene) was exactly weighed by precision balance (Sartorius cubis MSE6.6S-000-DM) and was put into a 6 cm³ screw top tube. And then 0.6 mmol of phenylboronic acid (TCI) and 1.0 mmol of potassium carbonate (FUJIFILM Wako, for organic synthesis) were added. The screw top tube was filled with 5 cm³ of water:ethanol (1:1 in volume) and sonicated for a short period of time (ca., 1-2 min). After addition of 0.5 mmol of 4-bromobenzene, the tube was then placed in a thermostatic water bath by cool pump to 20 °C, and stirred for 2h. Then the reaction mixture was transferred into a 100 cm³ screw top tube by use of 20 cm³ of water, then added 2 cm³ of CDCl₃ (Eurisotop, 99.80% D, 0.03% TMS). The mixture was vigorously stirred and the CDCl₃ layer was dried over a small amount of Na₂SO₄. Then the solution of CDCl₃ was subjected to ¹H NMR to determine the yield. To check the reproducibility of the coupling reaction, we repeated the same reaction two times.

The following chart (Fig. S1) is an example of estimating the yield of biphenyl in the catalytic reaction for 30 min (see entry-11 in Table 1) by ¹H NMR.

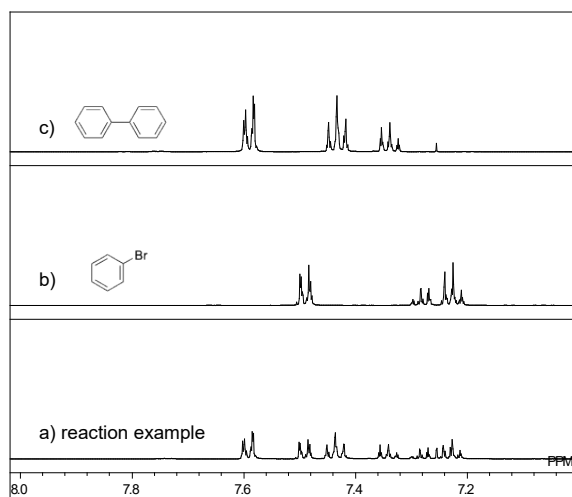


Fig. S1. ¹H NMR spectra of reaction mixture (a, reaction for 30 min), bromobenzene (b) and biphenyl (c) (CDCl₃, 600 MHz). In the spectrum of (a), the yield of the biphenyl was

estimated from the integration ratio of two peaks around 7.585 ppm (2x2H, ortho-proton on biphenyl) and around 7.485 ppm (2H, ortho-proton on bromobenzene).

2. Results and Discussion

2-1. Characterization data of products

BTC₇ :

NMR assays

White powder. ¹H NMR (CDCl₃, 600.17MHz, 298K): δ(ppm)=7.53 (s,2H, imidazole), 4.26 (t, J=7.8 Hz, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.86 (m, 4H), 1.39 (m, 2H), 1.32 (m, 4H), ¹³C NMR (CDCl₃, 150.92MHz, 298K): δ(ppm)=155.0, 151.6, 148.9, 140.7, 106.9, 47.1, 30.7, 29.7, 28.3, 27.9, 26.1.

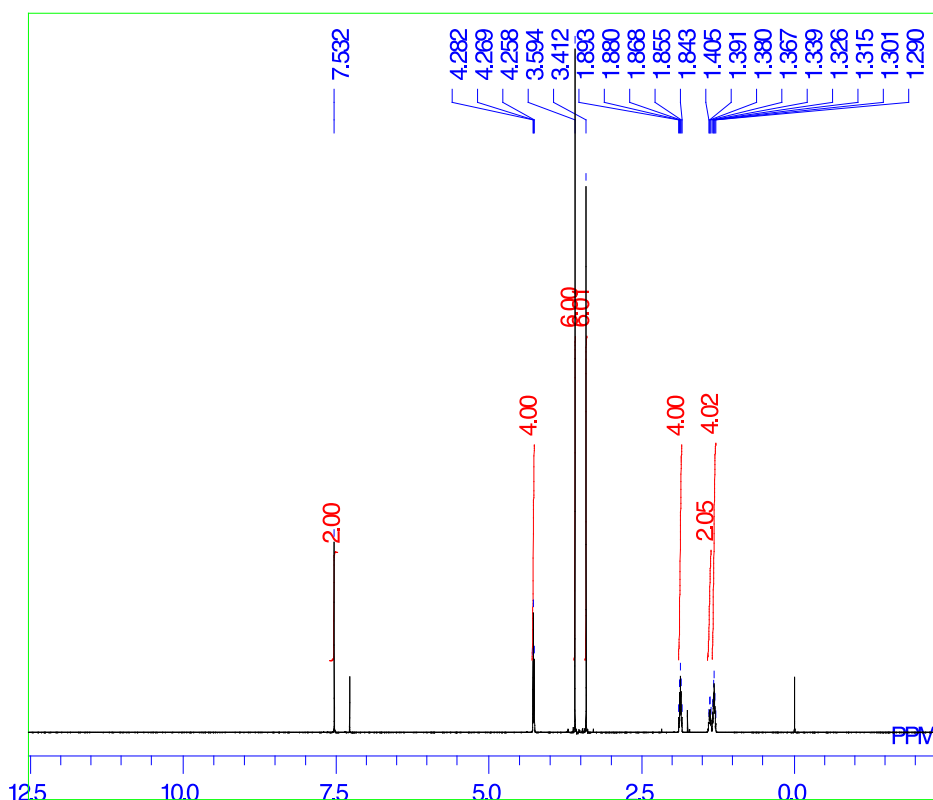


Fig. S2. ¹H NMR spectrum of BTC₇ (CDCl₃, 600 MHz).

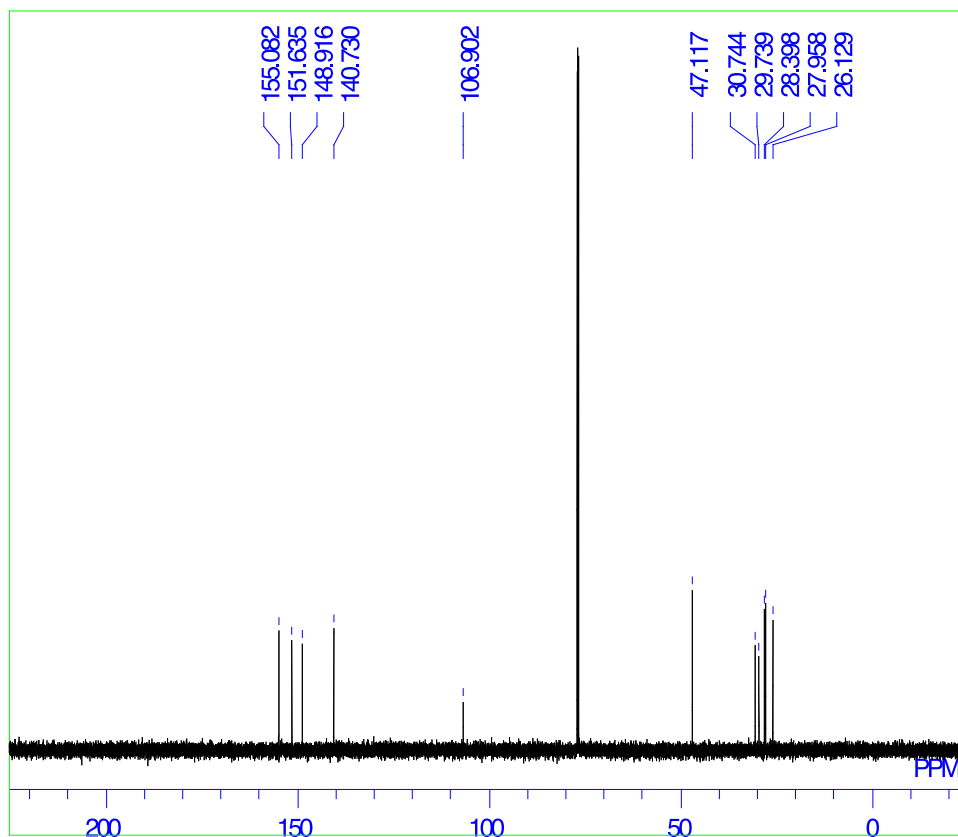


Fig. S3. ^{13}C NMR spectrum of BTC_7 (CDCl_3 , 150 MHz).

BTC₃ : White powder. ¹H NMR (D₂O/DCI=5:1 v/v, 600.17 MHz, 298K): δ(ppm)=7.35 (s,2H, imidazole), 2.87 (t, J=9.0 Hz, N-CH₂, 4H), 1.79 (s, 6H, N-CH₃), 1.52 (s, 6H, N-CH₃), 0.85 (quint, J=9.0 Hz, -CH₂, 2H), ¹³C NMR (D₂O/DCI=5:1 v/v, 150.92 MHz, 298K): δ(ppm)=153.9, 150.5, 140.3, 136.5, 106.3, 45.2, 31.1, 29.0.

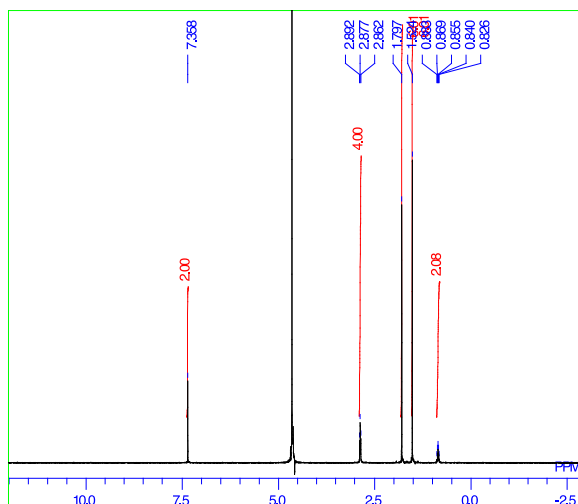


Fig. S4-1. ¹H NMR spectrum of BTC₃ (D₂O/DCI, 600 MHz).

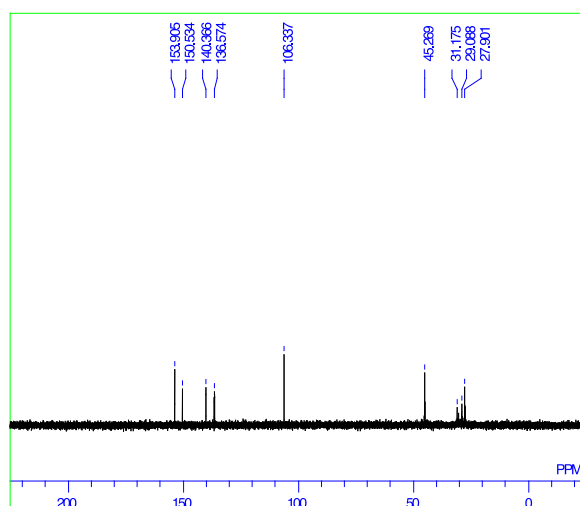


Fig. S4-2. ¹³C NMR spectrum of BTC₃ (D₂O/DCI, 150 MHz).

BTC₄ : White powder. ¹H NMR (CDCl₃/CD₃OD=5:1 v/v, 600.17 MHz, 298K): δ(ppm)=7.65 (s, 2H, imidazole), 4.34 (t, J=6.0 Hz, N-CH₂, 4H), 3.58 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.92 (m, -CH₂, 4H), ¹³C NMR (CDCl₃/CD₃OD=5:1 v/v, 150.92 MHz, 298K): δ(ppm)=155.0, 151.5, 148.8, 141.2, 106.7, 46.1, 29.6, 27.9, 27.4.

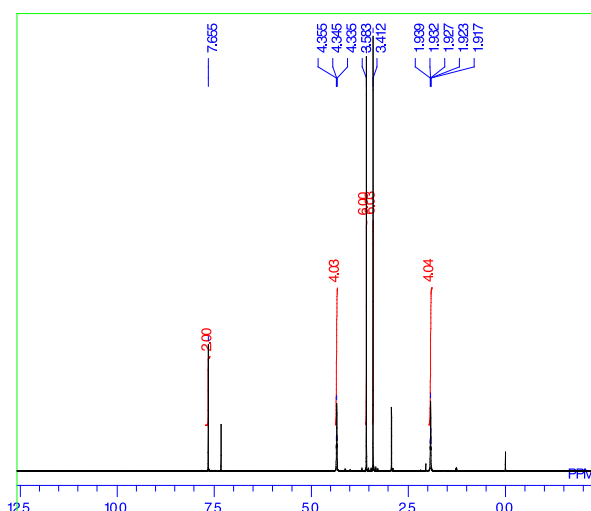


Fig. S5-1. ¹H NMR spectrum of BTC₄ (CDCl₃/CD₃OD, 600 MHz).

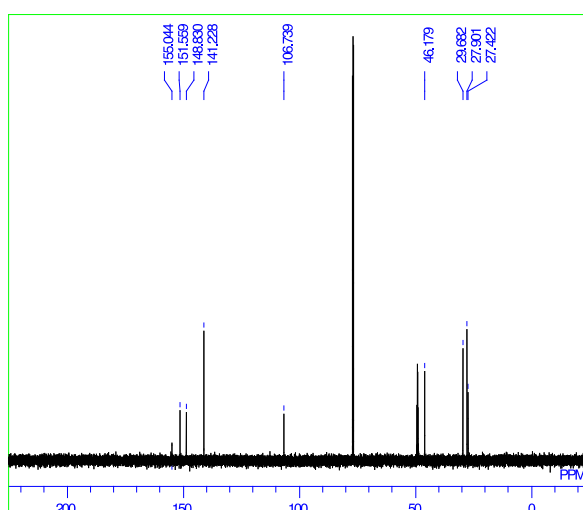


Fig. S5-2. ¹³C NMR spectrum of BTC₄ (CDCl₃/CD₃OD, 150 MHz).

BTC₅ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.57 (s, 2H, imidazole), 4.28 (t, J=6.0 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.95 (m, -CH₂, 4H), 1.37 (m, -CH₂, 2H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.9, 140.8, 106.8, 46.6, 30.1, 29.7, 27.9, 22.9.

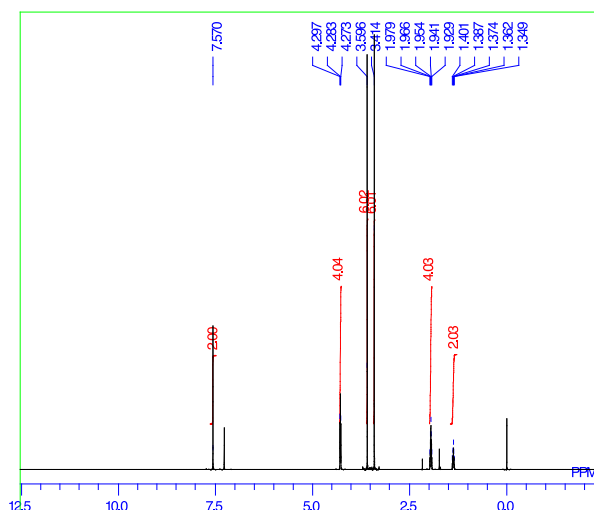


Fig. S6-1. ¹H NMR spectrum of BTC₅ (CDCl₃, 600 MHz).

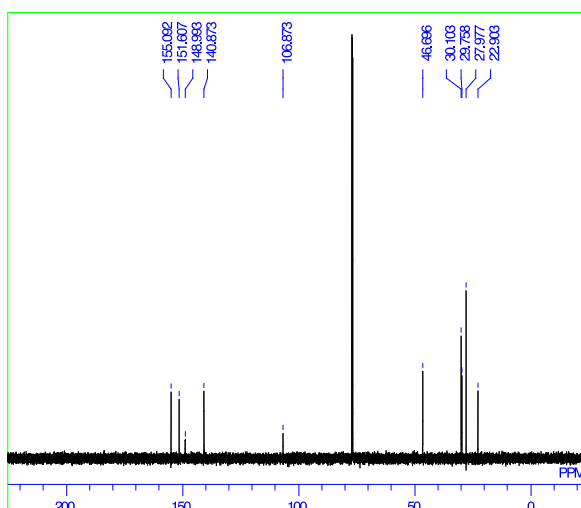


Fig. S6-2. ¹³C NMR spectrum of BTC₅ (CDCl₃, 150 MHz).

BTC₆ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.53 (s, 2H, imidazole), 4.27 (t, J=6.6 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.40 (s, 6H, N-CH₃), 1.88 (m, -CH₂, 4H), 1.37 (m, -CH₂, 4H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.9, 140.7, 106.8, 47.0, 30.6, 29.7, 27.9, 25.7.

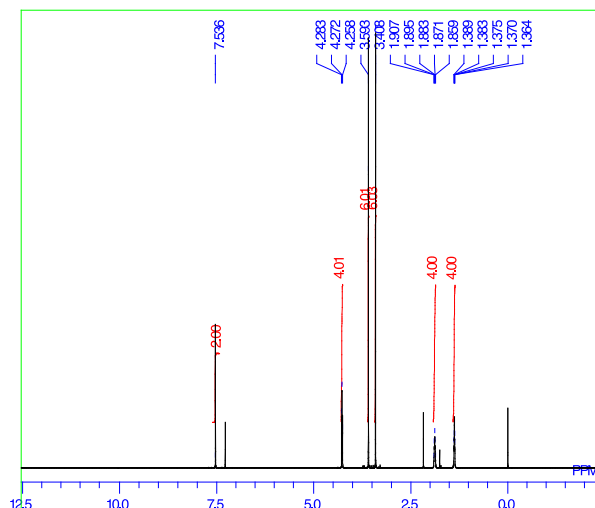


Fig. S7-1. ¹H NMR spectrum of BTC₆ (CDCl₃, 600 MHz).

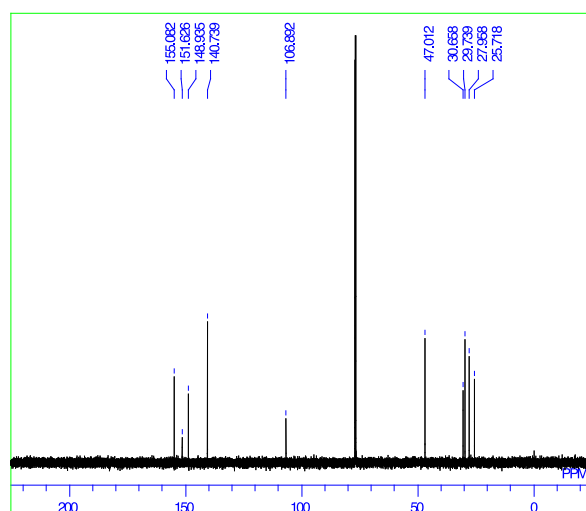


Fig. S7-2. ¹³C NMR spectrum of BTC₆ (CDCl₃, 150 MHz).

BTC₈ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.54 (s, 2H, imidazole), 4.27 (t, J=7.8 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.86 (m, -CH₂, 4H), 1.32 (m, -CH₂, 8H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.9, 140.7, 106.9, 47.1, 30.7, 29.7, 28.7, 27.9, 26.1.

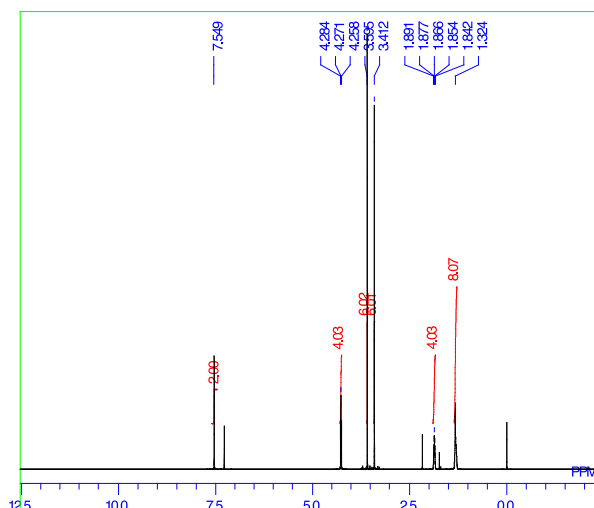


Fig. S8-1. ¹H NMR spectrum of BTC₈ (CDCl₃, 600 MHz).

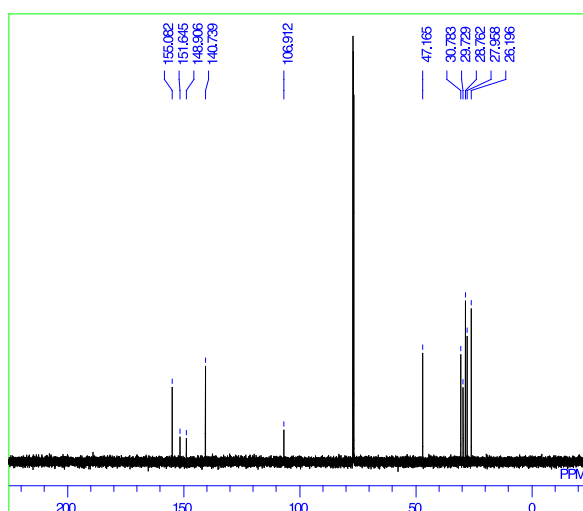


Fig. S8-2. ¹³C NMR spectrum of BTC₈ (CDCl₃, 150 MHz).

BTC₉ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.53 (s, 2H, imidazole), 4.27 (t, J=7.2 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.86 (m, -CH₂, 4H), 1.30 (m, -CH₂, 10H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.8, 140.7, 106.9, 47.2, 30.8, 29.7, 29.1, 28.8, 27.9, 26.2.

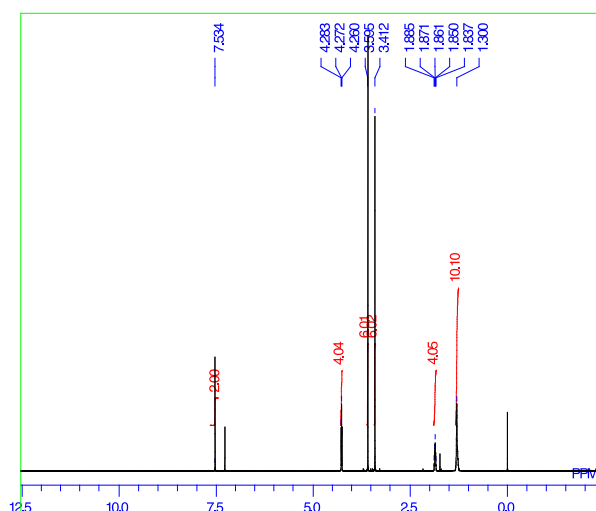


Fig. S9-1. ¹H NMR spectrum of BTC₉ (CDCl₃, 600 MHz).

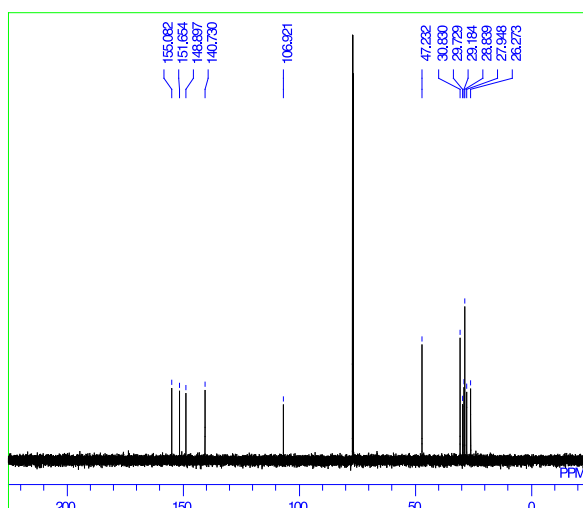


Fig. S9-2. ¹³C NMR spectrum of BTC₉ (CDCl₃, 150 MHz).

BTC₁₀ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.51 (s, 2H, imidazole), 4.27 (t, J=7.2 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.86 (m, -CH₂, 4H), 1.30-1.25 (m, -CH₂, 12H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.8, 140.7, 106.9, 47.2, 30.8, 29.7, 29.2, 28.9, 27.9, 26.3.

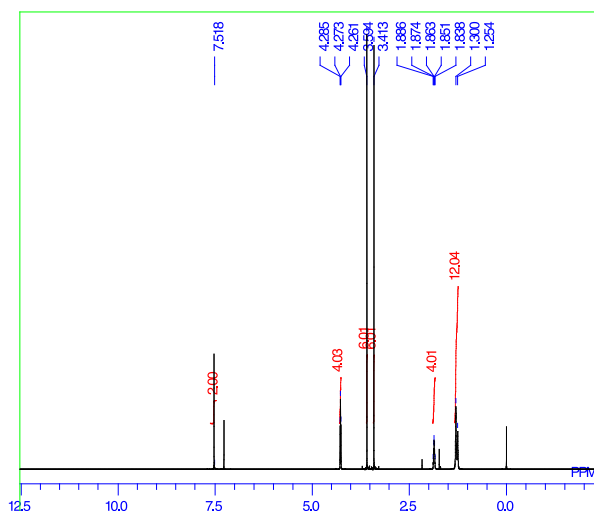


Fig. S10-1. ¹H NMR spectrum of BTC₁₀ (CDCl₃, 600 MHz).

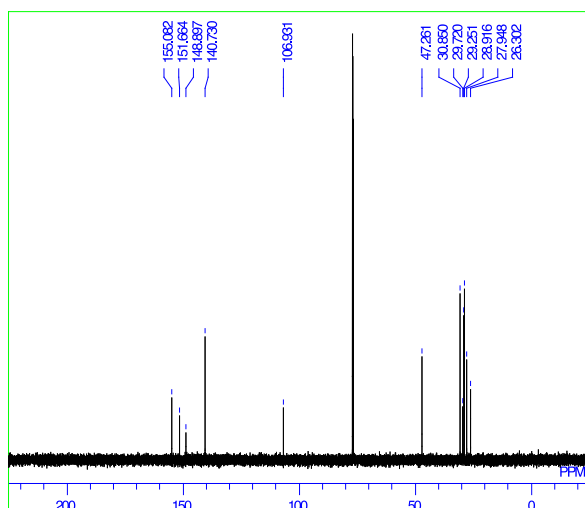


Fig. S10-2. ¹³C NMR spectrum of BTC₁₀ (CDCl₃, 150 MHz).

BTC₁₁ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.54 (s, 2H, imidazole), 4.28 (t, J=7.8 Hz, N-CH₂, 4H), 3.60 (s, 6H, N-CH₃), 3.42 (s, 6H, N-CH₃), 1.87 (m, -CH₂, 4H), 1.31-1.25 (m, -CH₂, 14H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.1, 151.7, 148.9, 140.7, 106.9, 47.2, 30.8, 29.7, 29.3, 28.9, 27.9, 26.3.

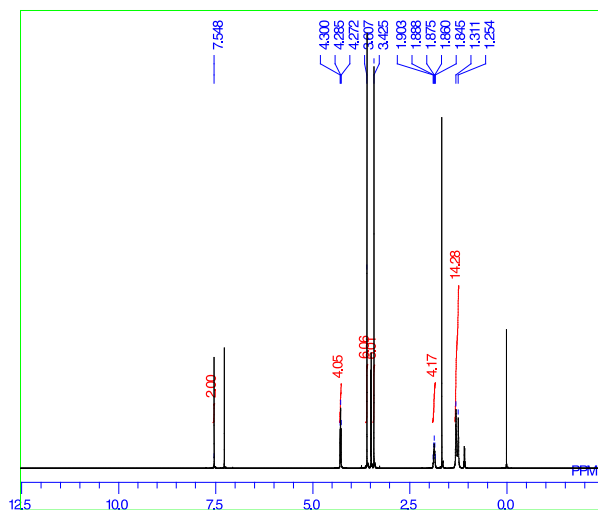


Fig. S11-1. ¹H NMR spectrum of BTC₁₁ (CDCl₃, 600 MHz).

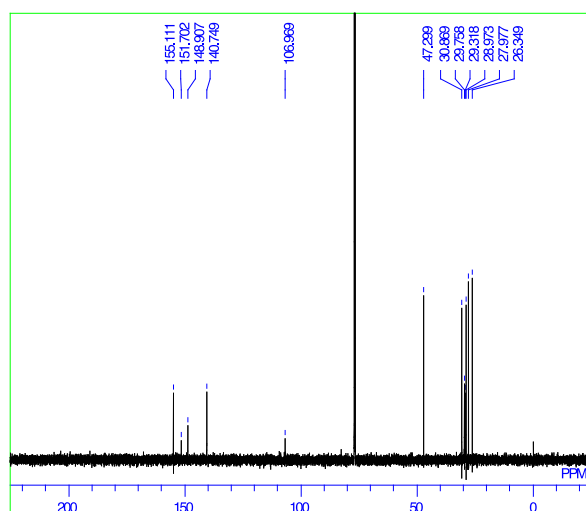


Fig. S11-2. ¹³C NMR spectrum of BTC₁₁ (CDCl₃, 150 MHz).

BTC₁₂ : White powder. ¹H NMR (CDCl₃, 600.17 MHz, 298K): δ(ppm)=7.53 (s, 2H, imidazole), 4.27 (t, J=8.4 Hz, N-CH₂, 4H), 3.59 (s, 6H, N-CH₃), 3.41 (s, 6H, N-CH₃), 1.86 (m, -CH₂, 4H), 1.30-1.23 (m, -CH₂, 16H), ¹³C NMR (CDCl₃, 150.92 MHz, 298K): δ(ppm)=155.0, 151.6, 148.8, 140.7, 106.9, 47.2, 30.8, 29.7, 29.3, 28.9, 27.9, 26.3.

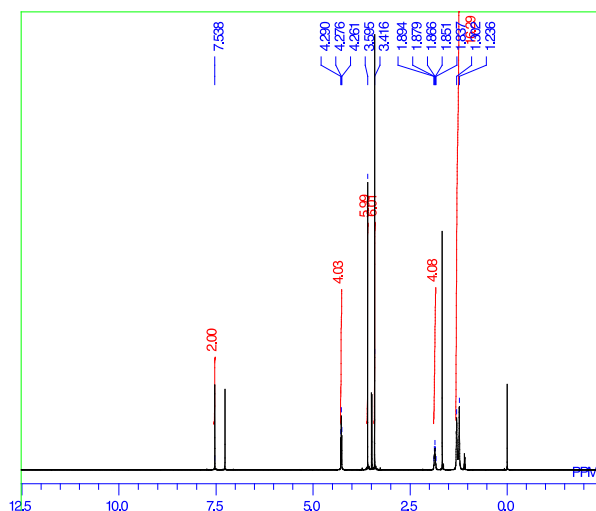


Fig. S12-1. ¹H NMR spectrum of BTC₁₂ (CDCl₃, 600 MHz).

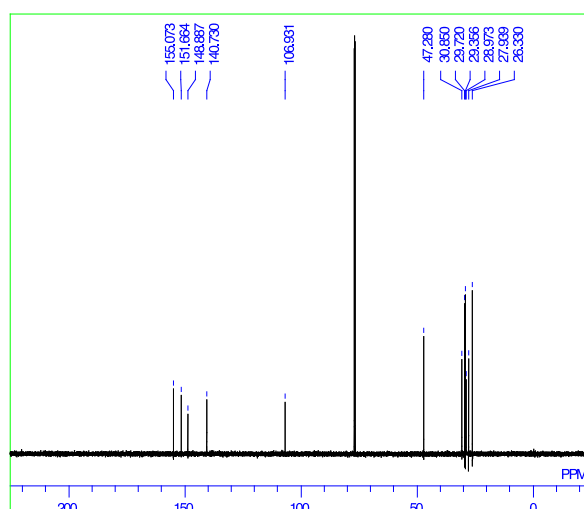


Fig. S12-2. ¹³C NMR spectrum of BTC₁₂ (CDCl₃, 150 MHz).

2-2. Nanostructured palladium/theophylline complex (PdBTC₇):

Elementary analysis

The component of PdBTC₇ was examined by elemental analysis and thermogravimetric analysis (TGA). PdBTC₇ (C₂₁H₂₈Cl₂N₈O₄Pd): calcd (%): C 39.79; H 4.45; N 17.68. Found: C 39.53; H 4.73; N 17.78. The weight loss from TGA-curve in the temperature range from 100 to 800°C was assigned to the organic fraction and chloride. The residue was 16.48%, which is good agreement with the theoretical value of Pd content (16.79%).

Table S1. Components of PdBTC₇ determined by elementary analysis and TGA.

Elements ^{a, b}	Calculated values (%)	Measured values (%)
C	39.79	39.53
H	4.45	4.73
N	17.68	17.78
Pd	16.79	16.48

[a] C, H, N contents were calculated by elemental analysis. [b] Pd content was determined by TG analysis.

Diffuse reflectance UV-Vis spectroscopy

The complex flowers formed once from theophylline ligand (BTC_7) and Pd(II) was insoluble in any solvents. So, we compared the powders of BTC_n and PdBTC_n by diffuse reflectance UV-VIS spectroscopy. The complex PdBTC_n showed new adsorption bands at 350 and 420 nm which are attributed to the chelate with Pd(II).

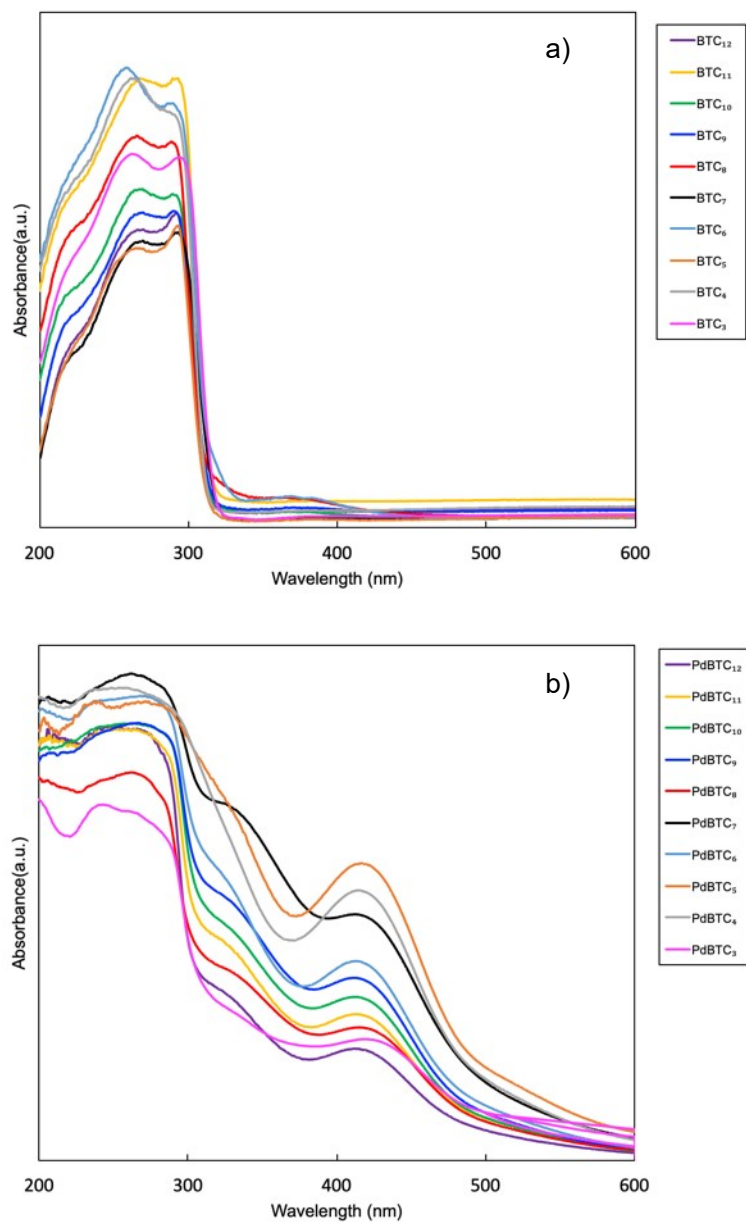


Fig. S13. Diffuse reflectance UV-Vis spectra of a) BTC_n , and b) PdBTC_n .

FT-IR spectroscopy

a) BTC₇ : FT-IR (KBr) ν C-H 3121, 2947 cm⁻¹, ν C=O 1703, 1659 cm⁻¹, b) PdBTC₇ : FT-IR (KBr) ν C-H 3090, 2927 cm⁻¹, ν C=O 1712, 1665 cm⁻¹.

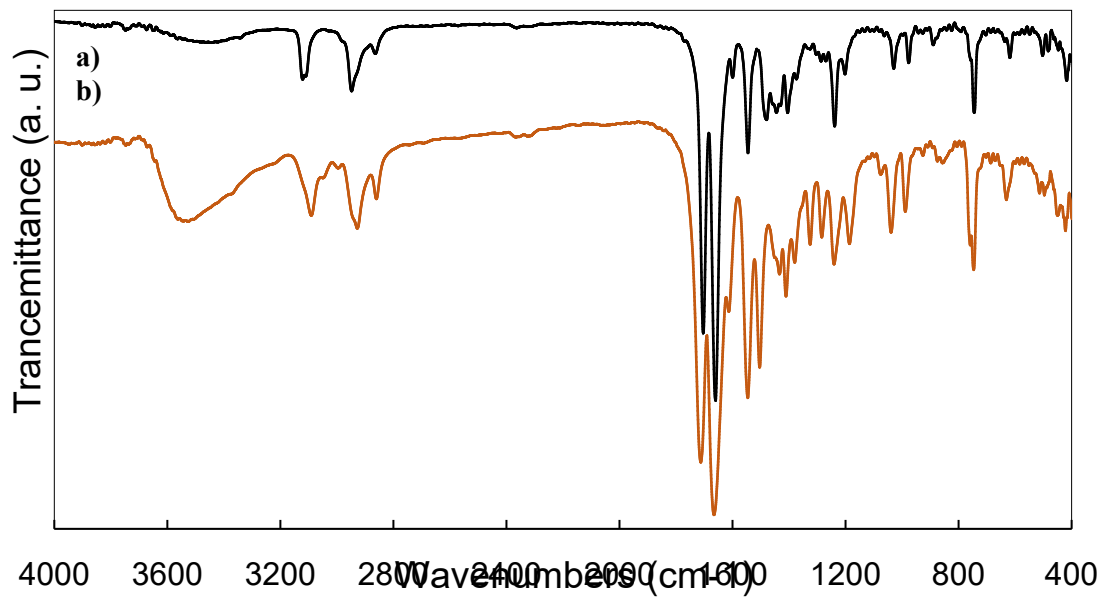


Fig. S14. FT-IR spectra of a) BTC₇ and b) PdBTC₇.

¹³C-CP/MAS NMR

BTC₇ : ¹³C-CP/MAS NMR (100.53MHz, 298K): δ(ppm)=154.2, 149.6, 148.1, 144.6, 140.5, 105.7, 47.0, 32.6, 28.4, 23.6, 21.1, PdBTC₇ : ¹³C-CP/MAS NMR (100.53MHz, 298K): δ(ppm)=153.7, 151.0, 147.3, 142.5, 108.2, 45.5, 33.2, 28.2, 23.3.

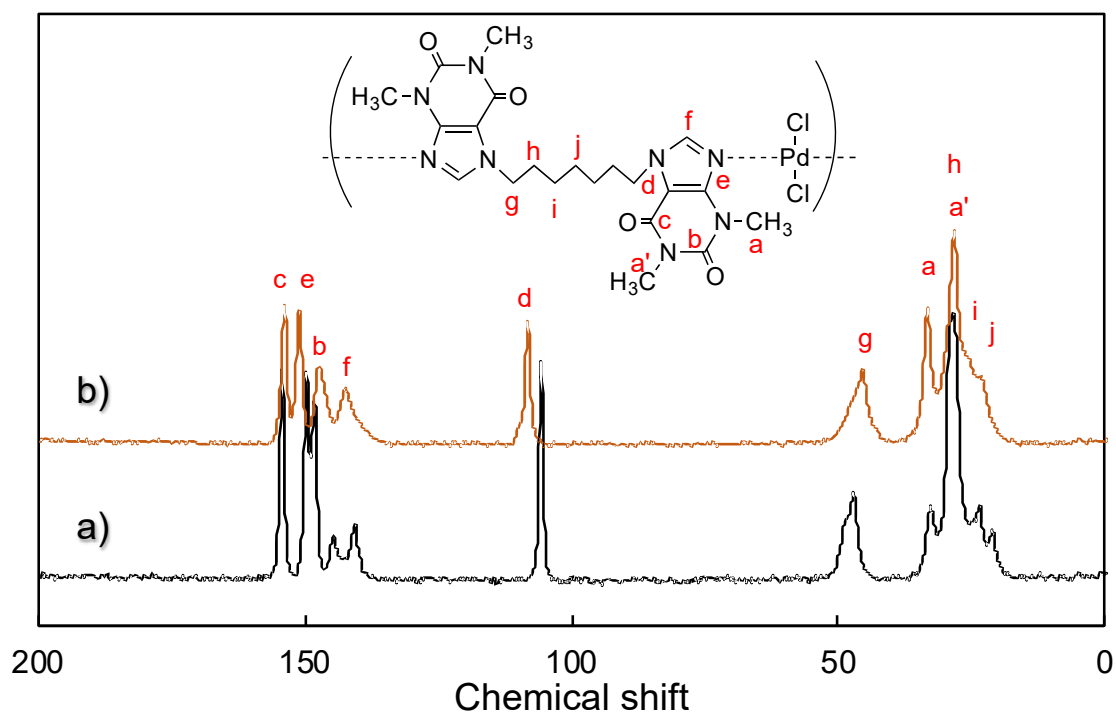


Fig. S15. Solid state ¹³C-CP/MAS NMR (100.53 MHz) spectra of a) BTC₇ and b) PdBTC₇.

XPS spectra

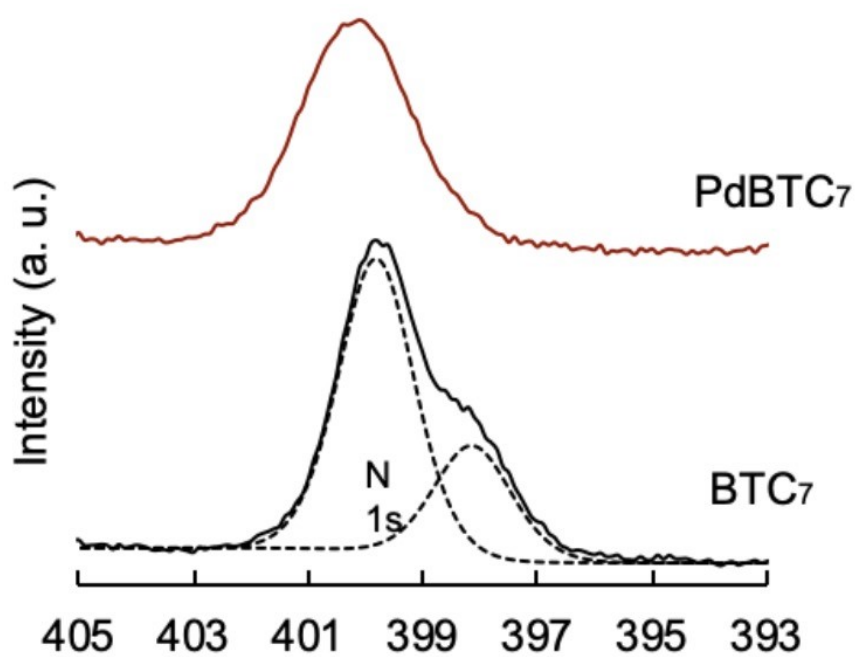


Fig. S16. High resolution XPS spectroscopy of N1s bonding energy of the ligand of BTC_7 and the complex of PdBTC_7 .

SEM images of the complexes PdBTC_n (n = 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12)

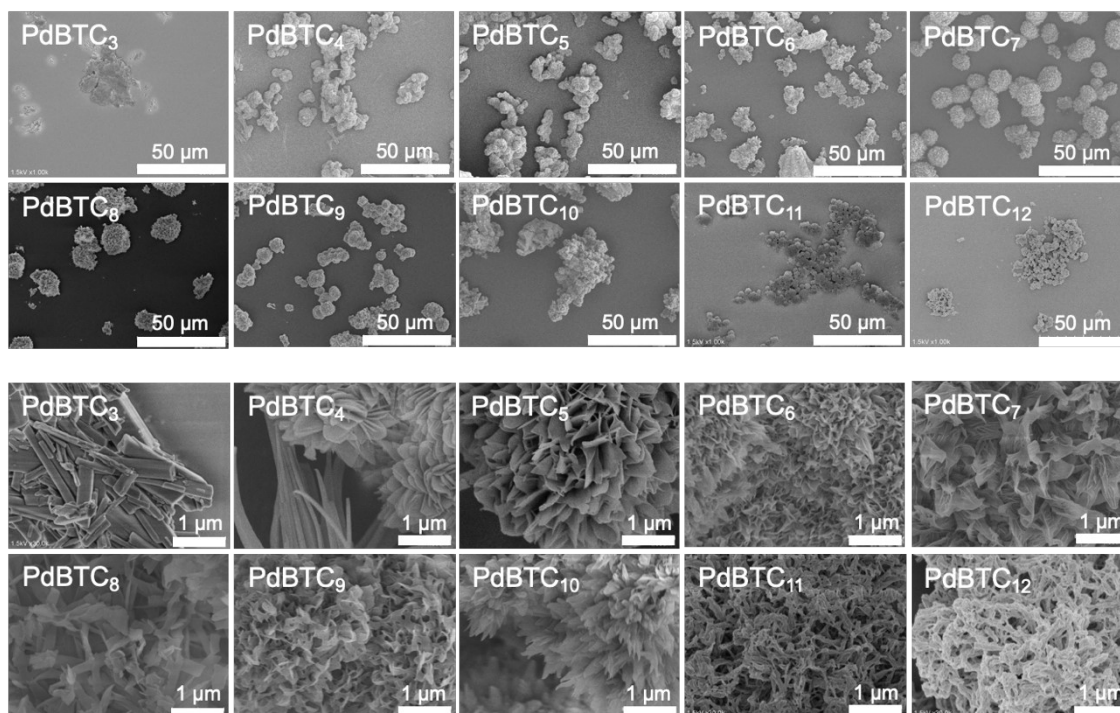


Fig. S17. SEM images of the complexes PdBTC_n (n=3-12) obtained from the complexation-driven self-assembly in solution containing PdCl₂ and BTC_n.

X-ray powder diffraction (XRD) measurements

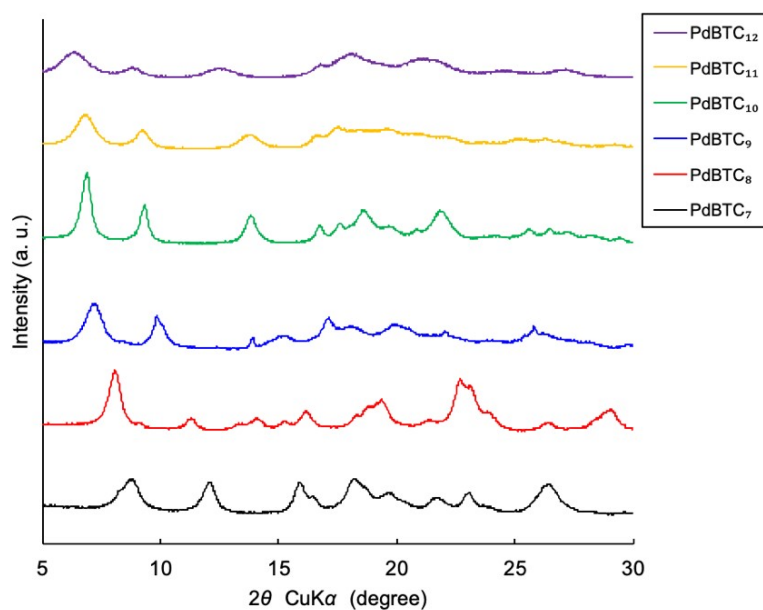


Fig. S18. XRD spectra of the as-prepared microflowers of PdBTC_n (n=7-12). The peaks appeared in the smaller diffraction angle ($2\theta < 10^\circ$) indicate that there are layered structures with long range period in the assemblies. This should be related to the arrangement of the alkyl chains (See Fig. S19).

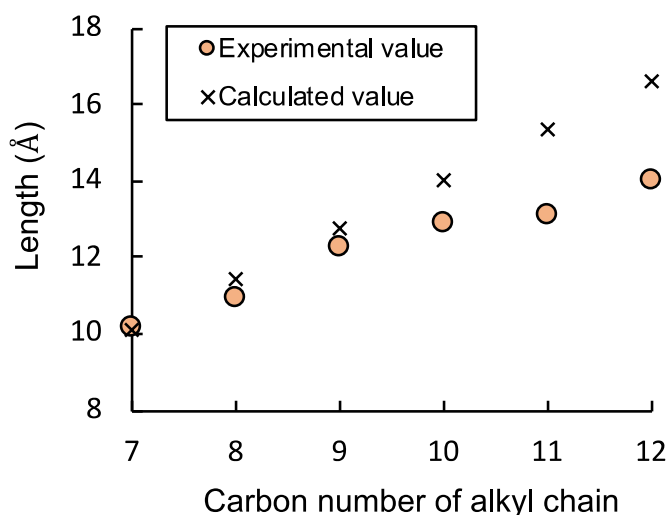
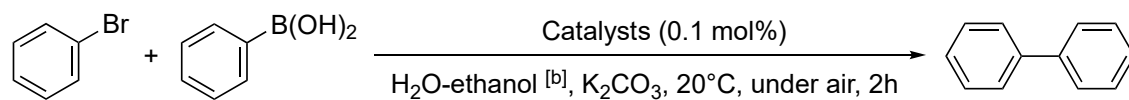


Fig. S19. Plot of the spacing data obtained from XRD of PdBTC_n (n=7-12) (Figure S18, the diffraction peak in the smallest angle) and the calculated length of alkyl chains against to the carbon number of the alkyl chain. The spacing increases with increasing the length of alkyl chain. This relationship suggests that the petal-like nano ribbons on the micro-flowers were composed of layered structures where the alkyl chains fold along two-dimensions to form layered surface.

2-3. Catalysis of PdBTCn in Suzuki-Miyaura coupling reactions

Table S2. Catalytic activity of PdBTCn (n=3-12) in the coupling of bromobenzene with phenylboronic acid.^[a]



Entry	Catalysts	Yield ^[c] (%)
1	PdBTC ₃	97
2	PdBTC ₄	98
3	PdBTC ₅	98
4	PdBTC ₆	97
5	PdBTC ₇	98
6	PdBTC ₈	98
7	PdBTC ₉	98
8	PdBTC ₁₀	98
9	PdBTC ₁₁	98
10	PdBTC ₁₂	98

[a] Reaction conditions: aryl halides(0.5 mmol), phenylboronic acid (0.6 mmol), base (1.0 mmol), solvent (5.0 mL). [b] H₂O:ethanol = 1:1. [c] Yields were determined by ¹H-NMR analysis.

2-4. Recyclability tests of PdBTC₇ for the Suzuki-Miyaura coupling reaction

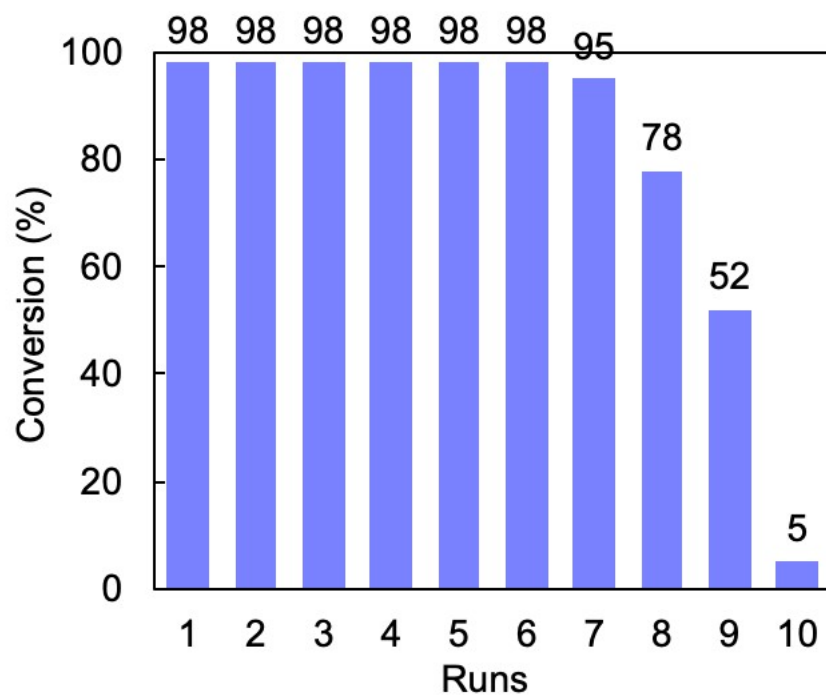


Fig. S20. Recyclability tests of PdBTC₇ for the coupling reaction of bromobenzene and phenylboronic acid. Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K₂CO₃ (1.0 mmol), 1.0 mol% PdBTC₇, solvent of H₂O:ethanol = 1:1 (5.0 mL).

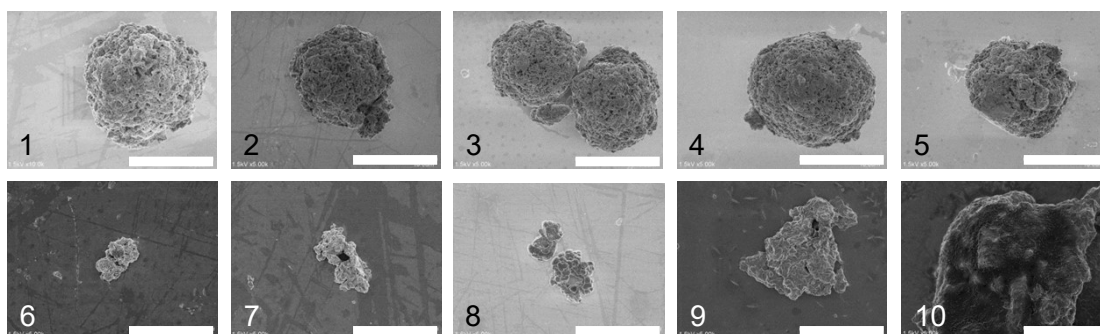
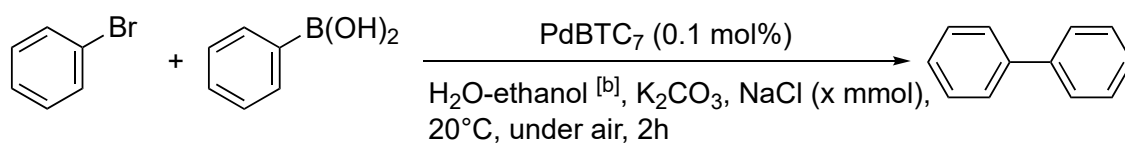


Fig. S21. SEM images of PdBTC₇ on the recyclability tests for the coupling reaction of bromobenzene and phenylboronic acid (scale bar : 10 μ m).

Table S3. Effect of the NaCl addition on the coupling of bromobenzene with phenylboronic acid.^[a]



Entry	NaCl (mmol)	Yield ^[c] (%)
1	0	98
2	0.05	98
3	0.5	98
4	1.0	97
5	2.0	96
6	5.0	69

[a] Reaction conditions: aryl halides(0.5 mmol), phenylboronic acid (0.6 mmol), base (1.0 mmol), solvent (5.0 mL). [b] H₂O:ethanol = 1:1. [c] Yields were determined by ¹H-NMR analysis.

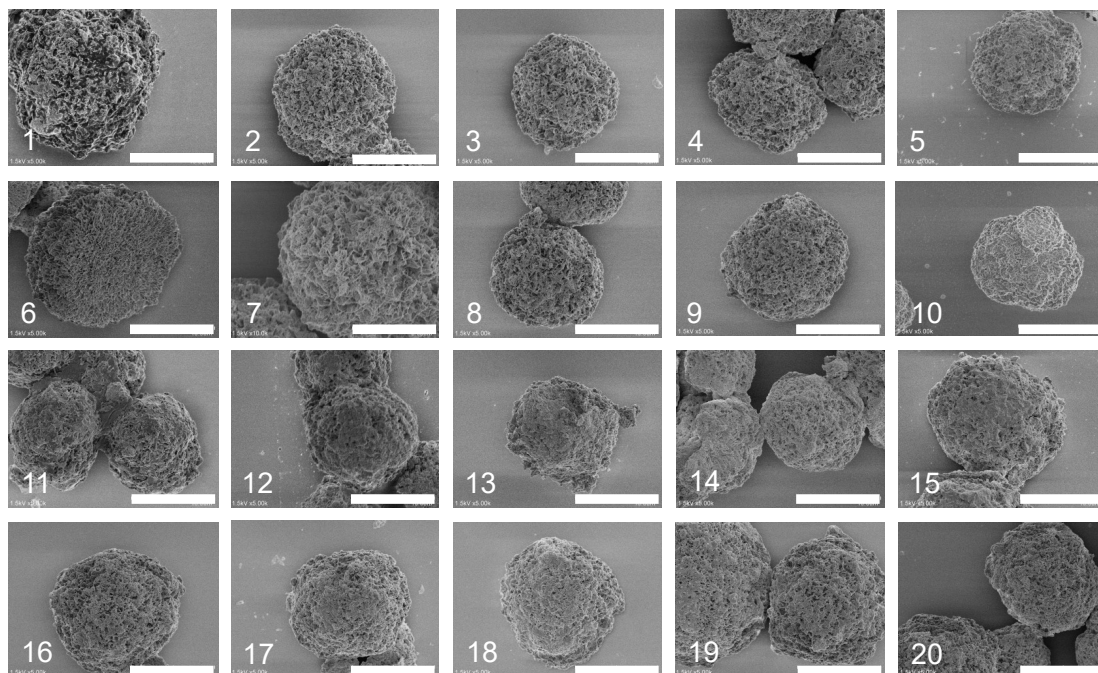


Fig. S22. SEM images of the powders of PdBTC₇ recovered from the recycle tests for the coupling reaction of bromobenzene and phenylboronic acid in the presence of NaCl (scale bar : 10 μm).

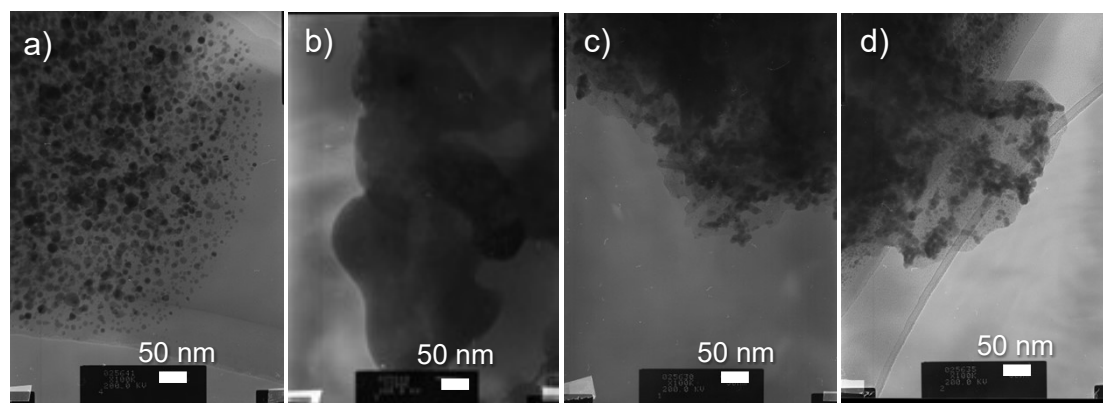


Fig. S23. TEM images of the powders of PdBTC₇ recovered from recycle tests in the presence or absence of NaCl for the coupling of bromobenzene and phenylboronic acid. a) PdBTC₇, b) PdBTC₇ after tenth reaction without NaCl, c) PdBTC₇ after tenth reaction in the presence of NaCl, d) PdBTC₇ after twentieth reaction in the presence of NaCl.

2-5. Hot filtrate test

The study on the heterogeneity of PdBTC₇ was carried out by hot filtrate test.[2-4] After reaction (Table 1, entry 21), the catalyst was filtrated off by membrane filter. To the filtrate, *p*-bromotoluene, phenylboronic acid and K₂CO₃ were added and this mixture was stirred at 50°C for 2 h. But no *p*-phenyltoluene was identified. This suggested that no leaching of the palladium species from PdBTC₇.

3. References

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