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SYNTHESIS, STRUCTURE, AND FLUORESCENT PROPERTIES OF [2.1.2.1]METACYCLOPHANE CONTAINING 2-(9-ANTHRYL)IMIDAZOLES

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Abstract – The Albright–Goldman oxidation of [2.1.2.1]metacyclophane ([2.1.2.1]MCP, **2**) containing hydroxy groups at the bridge yielded [2.1.2.1]MCP tetraone **3**. The subsequent condensation reaction of 9-anthraldehyde afforded 2-(9-anthryl)imidazole-annulated [2.1.2.1]MCP **3**. The UV and fluorescence spectra and their influence of sodium and lithium ion of the [2.1.2.1]MCP 2-(9-anthryl)imidazole adduct **4** were reported.

INTRODUCTION

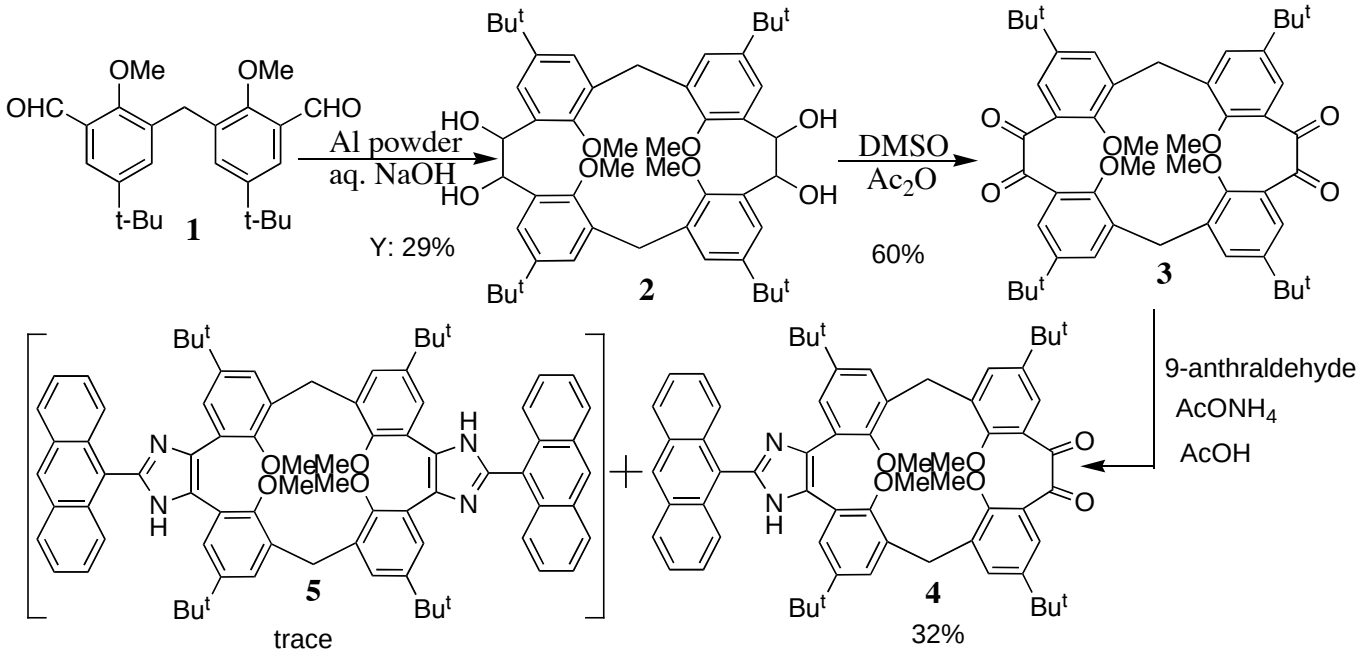
Lophine, 2,4,5-triphenylimidazole, is a chemoluminescent compound[1,2] that has been used for the analysis of some metal ions[3] and chlorinated compounds. In addition, 2,4,5-triarylimidazole derivatives are strongly fluorescent chromophores that are applied as the fluorescent moieties of functionalized molecules. Some examples of this application are the photochromic compounds that contain diarylethene derivatives,[4] clathrate crystals that are constructed with imidazole derivatives, and many types of organic molecules whose emission intensities and wavelengths are influenced by the presence of guest molecules.[5]

On the other hand, investigations have revealed that calixarenes, namely, [1_n]metacyclophanes (MCPs), can act as valuable host molecules for metal cations[6] and neutral molecules.[7] This is because they are produced by a one-step reaction and can be functionalized at their lower and upper rims.[8] We have previously reported a novel single-step synthesis of MCPs via the pinacol coupling of dialdehyde derivatives.[9] The synthesized MCPs had four hydroxyl groups located at the exo-position of the bridge moiety. Further, we have been investigating an application of the pinacol coupling reaction for preparing calixarene analogs and for the pinacol rearrangement of [2.1.2.1]MCP **2**.[10] In this study, we have investigated the Albright–Goldman oxidation of tetrahydroxy[2.1.2.1]MCP **2** and the annulation of the 2-(9-anthryl)imidazole moiety at the bridge position. The imidazole-annulated [2.1.2.1]MCP **4** contains 2,4,6-triarylimidazole moieties in its cyclophane skeleton. Therefore, it is expected to be a potential molecular probe that contains a fluorescent imidazole moiety and a calixarene-like cavity that could form a complex with organic molecules or alkali metal cations. It would be interesting to study the property of molecular recognition in [2.1.2.1]MCP **4** and its influence on the fluorescence spectra.

In this paper, we describe the synthesis, structure, and spectroscopic properties of [2.1.2.1]MCP **4**.

RESULTS AND DISCUSSION

The synthesis of [2.1.2.1]MCP **4** containing a 2-(9-anthryl)imidazole ring is shown in Scheme 1. The preparation of [2.1.2.1]MCP **2** is described in a previous study.[10]



Scheme 1

The oxidation of [2.1.2.1]MCP **2** was performed by the Albright–Goldman oxidation[11] using dimethylsulfoxide with acetic anhydride. The X-ray crystallographic structure of tetracarbonyl[2.1.2.1]MCP **3** is shown in Figure 1.[12]

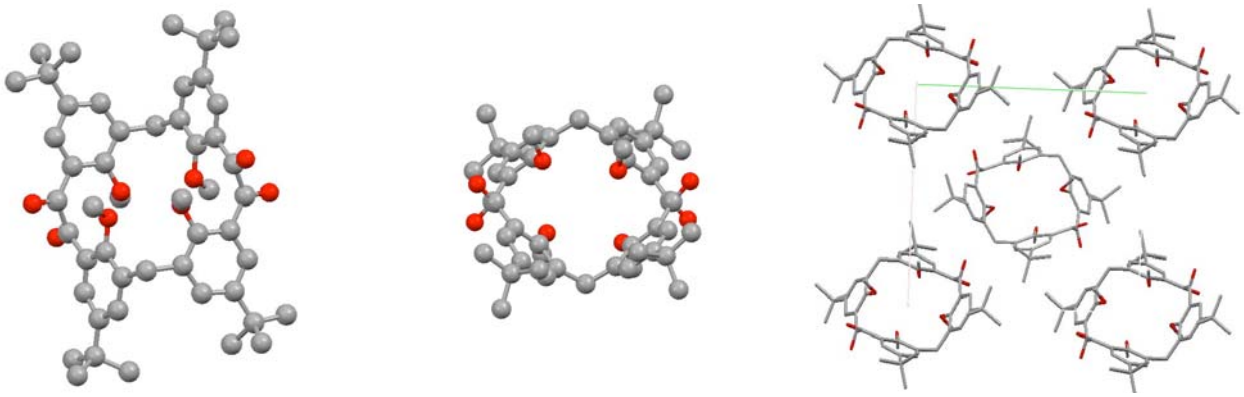


Figure 1. X-Ray crystallographic structure of [2.1.2.1]MCP **3**

The conformation of tetracarbonyl[2.1.2.1]MCP **3** was determined as the 1,2-alternate type in which the diphenylmethane units were oriented in alternate directions. The carbonyl groups of [2.1.2.1]MCP **3** were directed perpendicular to each other and the diameter of the cavity, measured as the distance between the carbonyl bridges, was 7.4 Å.

The 2-(9-anthryl)imidazole ring was introduced by treating tetracarbonyl[2.1.2.1]MCP **3** with 9-anthraldehyde in the presence of ammonium acetate. The annulation reaction of [2.1.2.1]MCP **3** yielded a monoimidazole-annulated [2.1.2.1]MCP **4** as the major product, but bis-annulated [2.1.2.1]MCP **5** was also detected in trace amounts. The perpendicularity of the dicarbonyl groups could decrease the reactivity of the second annulation reaction of [2.1.2.1]MCP **4**.

The ^{1}H-NMR spectrum of monoimidazole-annulated [2.1.2.1]MCP **4** is shown in Figure 2.

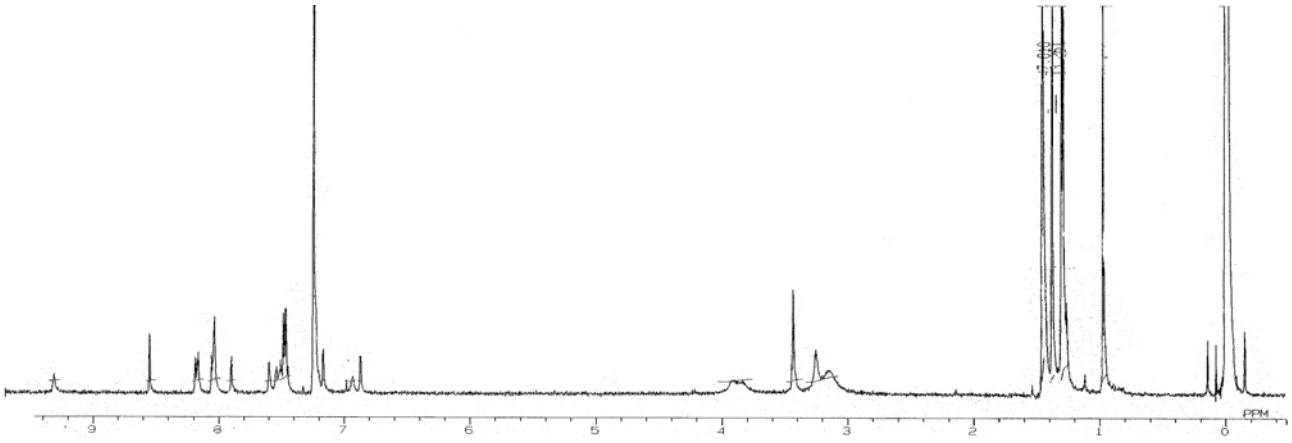


Figure 2. ^{1}H-NMR spectrum of [2.1.2.1]MCP **4** in $CDCl_3$

The peaks of the methylene bridge appear as a broad doublet (3.8–4.0 ppm), which suggests the conformational flexibility of [2.1.2.1]MCP **4**. The methoxy groups of [2.1.2.1]MCP **4** appeared as a broad multiplet, and the dynamic NMR spectra in toluene-d_8 indicated sharper and more complex peaks of methoxy and methylene for the temperature range from RT up to 100 ˚C. These observations suggest that [2.1.2.1]MCP **4** assumes an unsymmetrical conformation in the stable condition.

The X-ray crystallographic structure of [2.1.2.1]MCP **4** is shown in Figure 3.

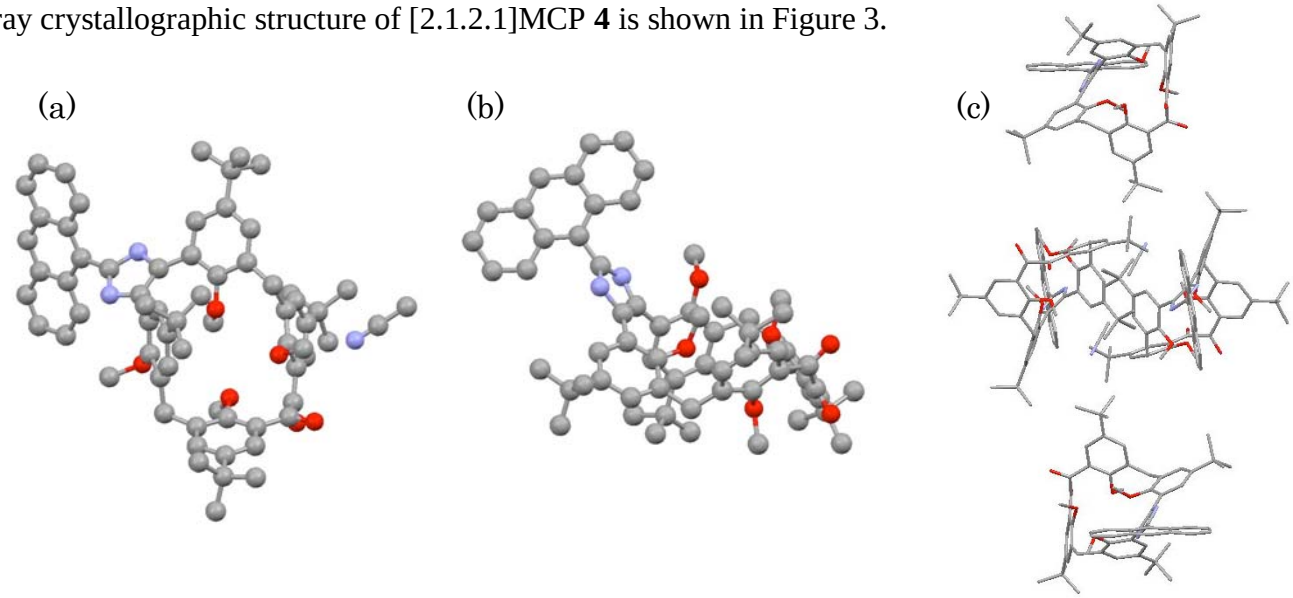


Figure 3. X-Ray crystallographic structure of [2.1.2.1]MCP **4**:
(a) front view, (b) side view, and (c) packing structure of **4**

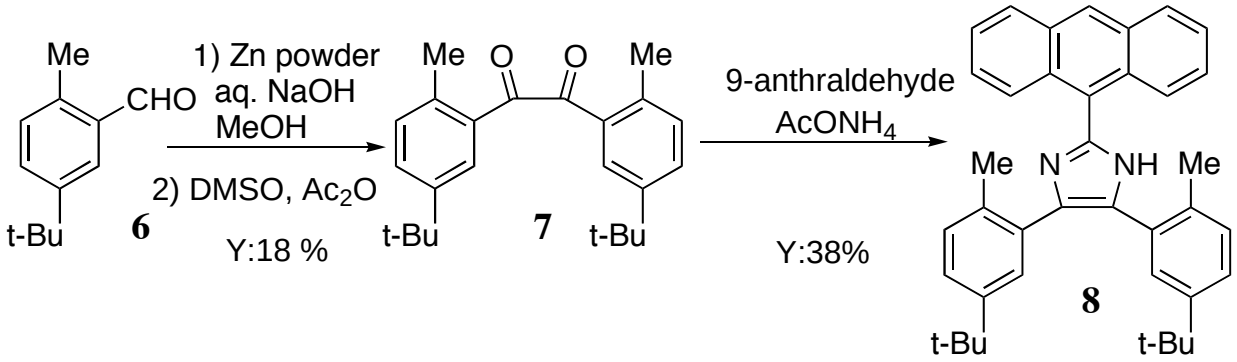
The conformation of [2.1.2.1]MCP **4** was determined to be of the partial-cone type by X-ray crystallography; in this conformation, one anisole unit was directed alternately with respect to the other anisole moieties. The ^{1}H-NMR spectrum also suggested this asymmetric conformation. The carbonyl groups were orthogonally oriented with regard to each other, and the low yield of bis-annulated [2.1.2.1]MCP **5** depended on this structure. The intramolecular hydrogen bonding between NH and methoxy oxygen and the intermolecular hydrogen bonding between the NH group of imidazole and the carbonyl carbon were observed using X-ray crystallography. The distance between the nitrogen atom of the NH group and the carbonyl oxygen was approximately 2.8 Å In the case of [2.1.2.1]MCP **4**, an acetonitrile group was present in the network space by the side of the cavity and not inside it. The dihedral angle between an anthracene and an imidazole unit was 54.8˚.

The UV-Vis absorption spectra and emission fluorescence spectra of [2.1.2.1]MCP **4** and 4,5-bis(-4-*tert*-butyltoluene)-2-(9-anthryl)imidazole **8**, which is the reference compound, are shown in Figures 4 and 5. The preparation of triarylimidazole **8** is shown in Scheme 2.

The absorption maxima ($\lambda_{max,UV}$) of [2.1.2.1]MCP **4** were observed at 365, 374, and 384 nm and those of triarylimidazole **8** were measured as 349, 369, and 386 nm in the MeCN solution. The peaks of [2.1.2.1]MCP **4** at 320 nm appear to be influenced by the extension caused by the π-conjugated system. The emission fluorescence spectra of [2.1.2.1]MCP **4** and triarylimidazole **8** were measured in MeCN and their emission maxima were observed at 492 and 490 nm, respectively. In the solid state, the emission maxima were detected at 484 and 474 nm for [2.1.2.1]MCP **4** and triarylimidazole **8**, respectively. In both cases, the relative emission intensity of [2.1.2.1]MCP **4** was higher than that of triarylimidazole **8**.

The higher emission intensity of [2.1.2.1]MCP **4** depends on the conformational stability due to its cyclic structure.

It has been reported that the measured emission maxima of triphenyl imidazoles in methanol and n-hexane are in the ranges of 385–585 nm and 385–490 nm, respectively.[1] These results suggest that the emission wavelength of triphenyl imidazoles were blue-shifted in polar solvents. Consequently, the emission wavelength of [2.1.2.1]MCP **4** can also be expected to influence the environment of the triarylimidazole moieties.



Scheme 2

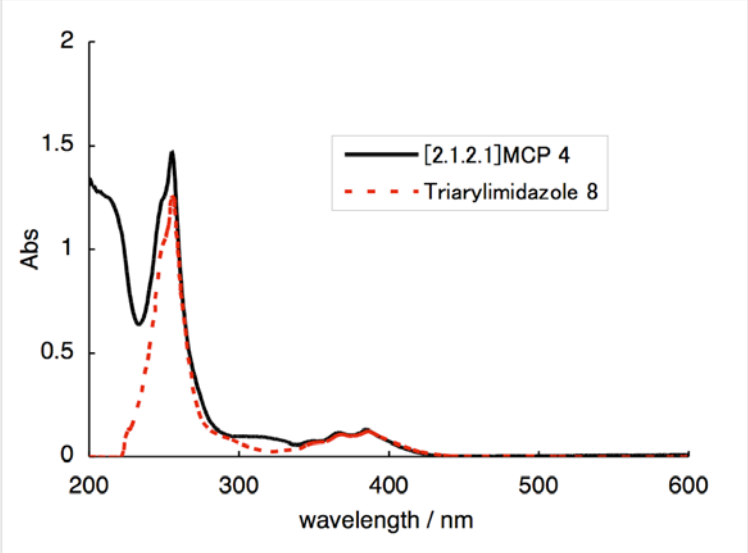


Figure 4. UV-Vis spectra of [2.1.2.1]MCP **4** and Triarylimidazole **8** in MeCN (1.7×10^{-5} mol/L)

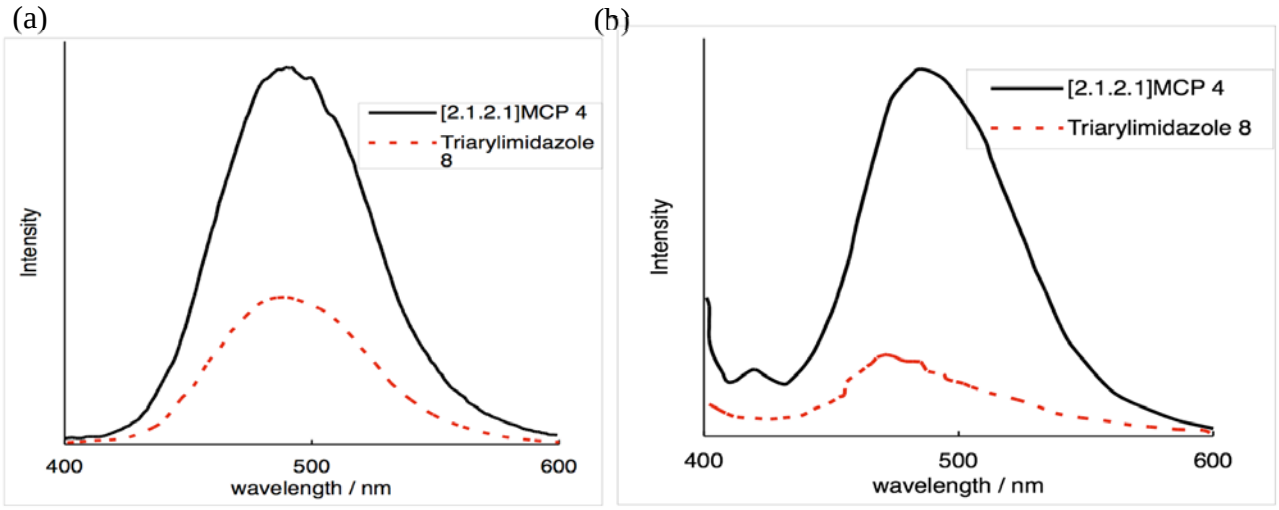


Figure 5. Emission fluorescence spectra of [2.1.2.1]MCP **4** and triarylimidazole **8** using an excitation wavelength of 384 nm (a) in MeCN (1.7×10^{-5} mol/L) and (b) in the solid state

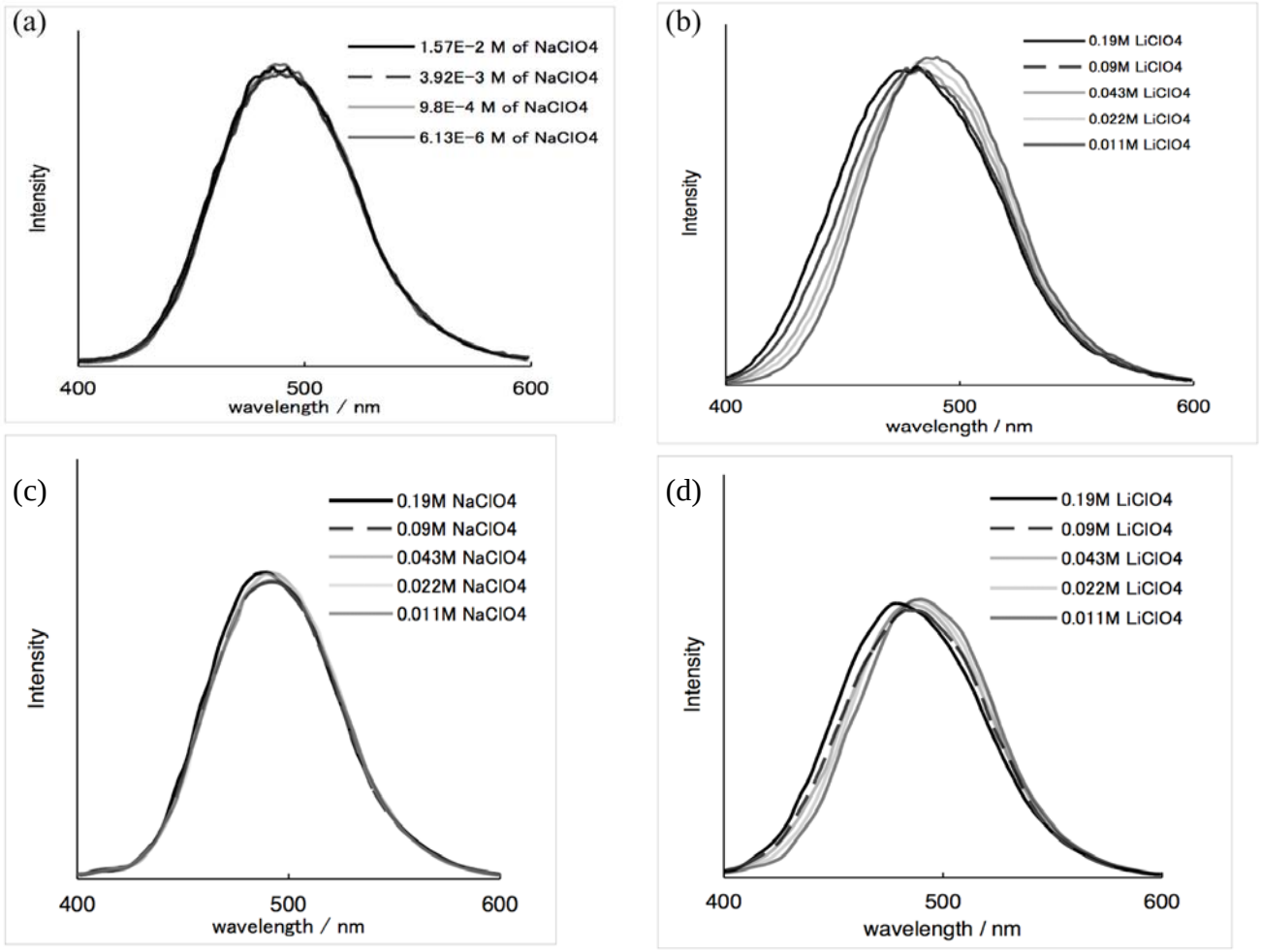


Figure 6. Emission fluorescence spectra of [2.1.2.1]MCP **4** and triarylimidazole **8** containing $NaClO_4$ or $LiClO_4$ for λ_{ex} = 384 nm in MeCN: (a) **4** in the presence of $NaClO_4$, (b) **8** in the presence of $NaClO_4$, (c) **4** in the presence of $LiClO_4$, and (d) **8** in the presence of $LiClO_4$

The emission fluorescence spectra of [2.1.2.1]MCP **4** and triarylimidazole **8** in the presence of $LiClO_4$ and $NaClO_4$ are shown in Figure 6.

The measurements were performed in MeCN at 1.7×10^{-5} M of [2.1.2.1]MCP **4** or triarylimidazole **8** in the presence of $NaClO_4$ or $LiClO_4$ (from 10^{-6} to 10^{-1} M). In the case of $KClO_4$, the fluorescence spectra could not be measured due to saturation and precipitation.

Although little change was determined in both the cases of [2.1.2.1]MCP **4** and triarylimidazole **8** in the presence of $NaClO_4$, the blue shift of the emission wavelength of both [2.1.2.1]MCP **4** and triarylimidazole **8** was detected with an increase in the amount of $LiClO_4$; these shifts were identical (–5 nm).

These results suggest that the imidazole moiety of [2.1.2.1]MCP **4** and triarylimidazole **8** can form a complex with the lithium ions and not with the sodium ions in the MeCN solution. This complex probably depends on the steric repulsion with anthracene and not on the cyclic structure since triarylimidazole **8** also show a blue shift of the emission wavelength; however, this hypothesis is not supported by substantial evidence with regard to the complexation process.

CONCLUSION

The triarylimidazole moiety is considered to be a strongly fluorescent chromophore and we applied it as a fluorescent chromophore unit for an ion-recognition probe in a macrocyclic compound. Tetracarbonyl[2.1.2.1]MCP **3** was prepared by the oxidation of tetrahydroxy[2.1.2.1]MCP **2**, and the annulation of tetracarbonyl[2.1.2.1]MCP **3** with 9-anthrylaldehyde yielded monoimidazole-annulated [2.1.2.1]MCP **4**. The X-ray crystallographic studies of [2.1.2.1]MCP **4** indicated that the intermolecular hydrogen bonding forms a clathrate network system and that an MeCN molecule exists in the interspace and not in the cavity of [2.1.2.1]MCP **4** as the clathrate compound.

The fluorescence emission of [2.1.2.1]MCP **4** was higher than that of the reference compound triarylimidazole **8** due to the conformational stability. Moreover, in the presence of lithium ions, the blue shift of the emission wavelength was observed in both the cases of [2.1.2.1]MCP **4** and **8**; however, no shift or change in the emission intensity was observed in the presence of sodium ions. These results suggest that [2.1.2.1]MCP **4** could form a complex with lithium ion at imimazol unit, not cyclic structure; however, the details of the complexation process and complexation constants are yet to be discovered.

In this paper, we have made the first attempt at introducing triarylimidazoles in a macrocyclic compound. However, there is still scope for improving the functionalization and molecular design of triarylimidazole-annulated MCP, the simple synthesis process, and the fluorescence emission. In addition,

it is expected that the clathrate complex of [2.1.2.1]MCP **4** will serve as supporting evidence for the potential of this complex as a novel fluorescence probe for metal ion or organic molecules.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H-NMR spectra were recorded at 400 MHz on a JEOL EX400 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured on Perkin Elmer Spectrum-One FT-IR spectrometer. Mass spectra were obtained on a JMS-DX303HF Mass spectrometer. UV spectra and fluorescent spectra were measured by Hitachi U-3210 spectrophotometer and Shimazu RF−540 Spectrofluorophotometer, respectively. Elemental analyses were carried out with Yanaco CHN Corder MT-6. X-ray diffraction was measured with a Rigaku AFC7R.

Preparation of 5,12,20-tetra-*tert*-butyl-8,15,23,30-tetramethoxyl[2.1.2.1]metacyclophane-1,2,16,17-tetraone (**3**).

Preparation of 5,12,20,27-tetra-*tert*-butyl-1,2,16,17-tetrahydroxy-8,15,23,30-tetramethoxy-[2.1.2.1]metacyclophane (**2**) has been described previously. [1]

After a mixture of acetic anhydride (2.0 mL, 19.7 mmol) and dry DMSO (14.0 mL) was stirring for 3 h at rt under nitrogen, a solution of **2** (170 mg, 0.21 mmol) in dry DMSO (4.0 mL) was added to the mixture at rt. After the mixture was stirred for 24h at rt under nitrogen atmosphere, cold water (40 mL) and aq. NH_3 solution (1.0 mL) was added to it and the mixture was extracted with $CHCl_3$ (60 mL×4). The extract was washed with water, dried over $MgSO_4$ and evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel (Waco-gel, C-200, eluent; hexane/EtOAc, 3/1) and recrystallized from hexane, to afford **3** (81.4 mg, 48%).

3: colorless prisms; mp 338.7-340.1 ˚C; FT-IR 1003, 1214, 1480, 1651, 1660, 2958 cm^{-1}; UV-Vis (MeOH) 259 (ε 1125), 313 (ε 3056); ^{1}H-NMR (400MHz, toluene-d_8) δ 1.26 (s, 36H), 3.32 (s, 12H), 3.91 (br, 4H), 7.52 (d, $^2J_{HH}$ = 2.44Hz, 4H), 7.75 (d, $^2J_{HH}$ = 2.4Hz, 4H); MS (TOF) *m/z* 815 (M^++Al). Ana. Calcd for $C_{50}H_{60}O_8$+H_2O: C, 74.44; H, 7.69. Found: C, 74.55; H, 7.85%.

Imidazole ring formation on tetracarbonyl[2.1.2.1]MCP 3.

18-(9-Anthryl)-5,12,23,30-tetra-*tert*-butyl-8,15,26,33-tetramethoxy[2.1]metacyclo[0](4,5)imidazolo-[0.1]metacyclophane-1,2-dione (4)

10,28-Di-9-anthryl-4,15,22,33-tetra-tert-butyl-7,18,25,36-tetramethoxy[1.1](3',3")-4,5-diphenyl-imidazolophane (5)

To a solution of **2** (153 mg, 0.19 mmol), NH_4OAc (484 mg, 6.3 mmol) in AcOH (6 mL) was added 9-anthraldehyde (120 mg, 0.58 mmol). After the mixture was refluxed for 6h under nitrogen, cold water (75 mL) was added to it and the mixture was extracted with $CHCl_3$ (60mL×4). The extract was washed with water, dried over dry $MgSO_4$ and evaporated *in vacuo*, leaving a residue, which was subjected to column chromatographed on silica gel (Waco-gel, C-200, eluent; hexane/AcOEt, 5/1) and recrystalized from MeCN to afford mono imidazole substituted [2.1.2.1]MCP **4** as 59 mg (32%) and bis imidazole substituted [2.1.2.1]MCP **5** was detected as under 1 mg.

4: orange prisms; mp 326.4-327.1 ˚C; FT-IR 1003, 1215, 1479, 1661, 2957, 3672 cm^{-1}; UV-Vis (CH_3CN) 299 (ε3194), 307 (ε3333), 332 (ε2917); ^{1}H-NMR (400MHz, $CDCl_8$) δ1.26-1.45 (m, 36H), 3.06-3.42 (m, 12H), 3.86 (brd, 4H), 6.85-6.88 (m, 1H), 7.13-7.15 (m, 1H), 7.43-7.55 (m, 6H), 7.58-7.62 (m, 1H), 7.88-7.90 (m, 1H), 8.02-8.07 (m, 2H), 8.14-8.20 (m, 1H), 8.54 (s, 1H) 9.32 (s, 1H); Anal. Calcd for $C_{65}H_{70}N_2O_6$: C, 80.05; H, 7.23; N, 2.87. Found: C, 79.88; H, 7.27; N, 2.85 %.

5: dark solid; ^{1}H-NMR (400MHz, $CDCl_8$) δ1.26 (s, 36H), 2.48-3.71 (s, 12H), 3.86 (br s, 4H), 7.22-8.54 (m, 26H).

Pinacole coupling and oxydation of 6

To a mixture of 4-*tert*-butyl-2-formyl-toluene **6** (3.8 g, 22 mmol), Zn powder (11.9 g, 181 mmol) and methanol (50 mL) was added 10% aq. NaOH solution (40 mL) under mechanical stirring. After being stirred for 1.5 h, CH_2Cl_2 (50 mL) was added to the mixture and stirred for 30 min. the mixture was filtered, and filtrate was extracted with CH_2Cl_2 (50 mL×3), washed with saturated aq. NaCl (50 mL×3), dried over $MgSO_4$, evaporated in vacuo, residue was washed with cold hexane, to afford diol (2.3 g, 59 % as dl and meso isomer radio is about 1 : 1, estimated by ^{1}H-NMR spectra) as white powder. After a mixture of Ac_2O (1.5 mL, 14.0 mmol) and dry DMSO (10 mL, 140 mmol) was stirring for 4 h at rt under nitrogen atmosphere, the diol (200 mg, 0.56 mmol) was added to the mixture at rt. After the mixture was stirred for 64 h at rt under nitrogen atmosphere, cold water (20 mL) and aq. NH_3 solution was added to it until

mildly alkaline and the mixture was extracted with CH_2Cl_2 (30 mL×3). The extract was washed with water saturated NaCl (30 mL×3), dried over $MgSO_4$ and evaporated *in vacuo,* leaving a residue, recrystallized from hexane, to afford 1,2-bis-2-(4-*tert*-butyltoluene)-ethane-1,2-dione **7** (59.6 mg, total yield of 18 %) as yellow solid.

7: yellow solid; mp 42.0~43.0 ˚C; FT-IR 830, 1193, 1669, 2909, 2958 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 1.25 (s, 18H), 2.62 (s, 6H), 7.28 (s, d, *J*=7.83 Hz, 2H),7.51 (dd, *J*=2.71 Hz, *J*=7.83 Hz, 2H), 7.71 (d, *J*=2.71 Hz, 2H); MS (EI) *m/z* 350 (M^+); Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 81.97; H, 8.75%.

Preparation of 4,5-bis(-4-tert-butyltoluene)-2-(9-anthryl)imidazole 8

To a solution of dion **7** (750 mg, 2.1 mmol), NH_4OAc (2.48 g, 32 mmol) in AcOH (10 mL) was added 9-anthraldehyde (443mg, 2.1 mmol). After the mixture was refluxed for 4h under nitrogen, cold water (50 mL) was added to it and the yellow solid was filtrated and wash water. The yellow solid was dried and subjected to column chromatographed on silica gel (Waco-gel, C-200, eluent; hexane/ethyl acetate, 5/1) and recrystalized with hexane, to afford 4,5-bis(-4-*tert*-butyltoluene)-2-(9-anthryl)imidazole **8** (475 mg, 38 %) as yellow needle.

8: yellow needle; mp 106.3-108.3 ˚C (hexane); FT-IR 731, 1223, 1361, 1669, 2967, 3735 cm^{-1}; ^1H-NMR (400MHz, $CDCl_8$) δ1.25 (s, 9H), 1.30 (s, 9H) 2.17 (s, 3H), 2.40 (s, 3H), 7.14 (d, J=7.82 Hz, 1H), 7.30-7.33 (m, 1H), 7.49-7.53 (m, 4H), 8.03-8.08 (m, 2H), 8.13-8.18 (m, 2H), 8.56 (s, 1H) 9.26 (s, 1H); MS (EI) *m/z* 536 (M^+); Anal. Calcd for $C_{39}H_{40}N_2$: C, 87.27; H, 7.51; N, 5.22, Found: C, 86.82; H, 7.49; N, 5.30 %.

X-Ray structure determination

Crystal data of 3: colorless prism, $C_{50}H_{60}O_8$, *M* =788.98, Monoclinic, space group *P* 2_1/n, a = 14.354(5) Å, *b* = 14.965(5) Å, *c* = 10.866(5) Å, *β*= 91.042(5)˚, V = 2333.7(16) $Å^3$, *Z* = 2, D_{calc} = 1.123 Mg/m^3, crystal dimension 0.25 x 0.20 x 0.20 mm. Data were measured on a Rigaku AFC 7R radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 6442 refrections (5349 unique) were collected using ω-2θ scan technique with in a 2θ range of 55.0˚. The structure was solved by direct methods (SIR92),[13] and refined a full-matrix least squares methods using CrystalStructure analysis software13 with 5349 observed refrections [I > 2σ(I)]. The final refinement converged to *R* = 0.073 and Rw = 0.13. CCDC 298137 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Crystal data of 4: colorless prism, $C_{65}H_{70}N_2O_6$, + C_2H_3N, M =1016.28, Monoclinic, space group P $2_1/n$, a = 17.685(5) Å, b = 24.83(1) Å, c = 14.741(4) Å, β = 105.27(2)°, V = 6245(3) Å^3, Z = 4, D_{calc} = 1.081Mg/m^3, crystal dimension 0.60 x 0.60 x 0.40 mm. Data were measured on a Rigaku AFC 7R radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 14340 refrections were collected using ω-2θ scan technique with in a 2θ range of 55.0°. The structure was solved by direct methods (SIR92),[13] and refined a full-matrix least squares methods using CrystalStructure analysis software13 with 5134 observed refrections [I > 2σ(I)]. The final refinement converged to R = 0.078 and Rw = 0.253. CCDC 635460 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

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