Rhomboid-shaped Organic Host Molecule with Small Binding Space. Unsymmetrical and Symmetrical Inclusion of Halonium Ions

<table>
<thead>
<tr>
<th>Journal</th>
<th><em>Dalton Transactions</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>DT-ART-12-2013-053629.R1</td>
</tr>
<tr>
<td>Article Type</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author</td>
<td>02-Feb-2014</td>
</tr>
<tr>
<td>Complete List of Authors</td>
<td>Suzaki, Yuji; Tokyo Institute of Technology, Saito, Takashi; Tokyo Institute of Technology, Ide, Tomohito; Tokyo Institute of Technology, Osakada, Kohtaro; Tokyo Institute of Technology, Chemical Resources Laboratory</td>
</tr>
</tbody>
</table>
Rhomboid-shaped Organic Host Molecule with Small Binding Space. Unsymmetrical and Symmetrical Inclusion of Halonium Ions

Yuji Suzaki, Takashi Saito, Tomohito Ide and Kohtaro Osakada*

A shape persistent rhomboid-shaped organic host molecule having two pyridyl unit was synthesized which induces the size selective halonium inclusion. Cl+ and Br+ are included to form unsymmetric and symmetric complex, while I+ does not form stable complex. The difference among the haloniums was ascribed to the matching (or mismatching) of the shape of the cavity and the guest ions. The complexation of the host molecule with other cations, such as Ag+, Pd2+, Zn2+ and H+ is also mentioned.

In this paper, we designed a cyclic organic host molecule composed of two pyridyl and two 1,2-dialkyl benzene units (cpeb) which is expected to have a similar N...N distance and a rigid structure, suited for complexation with haloniums. Here we report unique inclusion behavior of cpeb for the haloniums.

Results and discussion

Eq 1 depicts the synthesis of cyclic pyridylethynylbenzene (cpeb) by deprotection of -SiMe2{(CH2)3CN} group of 1 under basic condition followed by intramolecular Sonogashira-Hagihara cross-coupling reaction of 1. The palladium(II) complex, Pd(OCOCF3)2(cpeb), was obtained by reaction of Pd(OCOCF3)2 and cpeb in 70%. Fig. 1 shows molecular structures of cpeb and its complex with Pd(OCOCF3)2 guest determined by X-ray crystallography. Cpeb has crystal polymorph (orthorhombic, Cmce (no. 64) and Pbca (no.61)) depending on the recrystallization conditions (Fig. 1a, b). The crystal structure analyzed as Cmce (no. 64) has 4-fold symmetry axis in which all the atoms are located within a single plane (Fig. 1a) while the two pyridine rings in the structure analyzed as Pbca (no. 61) are parallel in the molecule with a 2-fold axis (Fig. 1b). Molecular structure of Pd(OCOCF3)2(cpeb) adopts square planar molecular geometry where pyridine units located at trans positions to Pd(II). Pd atom is located at the mid-point of the two nitrogen atoms. Distance between the nitrogen atoms of cpeb is 4.30 Å in both the structure (N1-N1* in Figure 1a and N1-N2 in Figure 1b).

Scheme 1. Structure of peb, bpeb and Yoshida's macrocycle.
Yoshida et al. selected macrocyclic molecule, a cycleny type azamacrocycles having two pyridine units and two 1,3-dialkyl benzene as the host and found its light-emitting inclusion complex with Sb(V)Cl$_5$. Cpeb is estimated to have much shorter N-N distance and smaller binding space than the meta-substituted cyclic host. N1-N1* distance of Pd(OCOCF$_3$)$_2$(cpeb) (4.09 Å) is shorter than the corresponding distance of cpeb, which is attributed to coordination of the Pd(II) ion.

UV-vis spectroscopy measurements revealed a remarkable bathochromic shift of cpeb ($\lambda_{\text{max}}$ = 319 nm) upon addition of Cl$^+$OTf$^-$ ($\lambda_{\text{max}}$ = 357 nm) and Br$^+$OTf$^-$ ($\lambda_{\text{max}}$ = 358 nm) (Figure 2a, Table 1). The shoulder peaks are observed at ca 400 nm in the spectra of the mixture of cpeb and X$^+$OTf$^-$ (X = Cl, Br). Negligible change was observed in the reaction of cpeb and I$^+$OTf$^-$.

Emission spectra also show the bathochromic shifts upon complexation of Cl$^-$ and Br$^-$. Excitation of the mixture of cpeb and Cl$^+$OTf at $\lambda_{\text{ex}}$ = 357 nm results in green emission ($\lambda_{\text{max}}$ = 508 nm) with Stokes shift of 1.00 eV and moderate quantum yield (\(\phi = 0.12\)), while cpeb shows emission at $\lambda_{\text{max}}$ = 403 nm with smaller Stokes shift (0.81 eV) (Figure 2b). The quantum yield from Cl$^-$(cpeb) (\(\phi = 0.12\)) is higher than that of Br$^-$(cpeb) (\(\phi = 0.05\)). The color change in light-emitting between before and after addition of X$^+$OTf$^-$ (X = Cl, Br) to the solution of cpeb is clear (Figure 2b, inset, $\lambda_{\text{ex}}$ = 365 nm). The lifetime of emission from the mixture of cpeb and Br$^+$OTf$^-$ ($\tau_0 = 10$ ns) is longer than that of cpeb ($\tau_0 = 6.5$ ns). The solid-state emission from cpeb ($\lambda_{\text{max}}$ = 403 nm, $\phi = 0.14$ (absolute)) is similar to that from the solution while the solid obtained by the evaporation of the mixture of cpeb and X$^+$OTf$^-$ (X = Cl, Br) is not emissive ($\phi < 0.01$ (absolute)).

HR-ESI-MS spectra obtained from the mixture of cpeb and Br$^+$OTf$^-$ in CH$_2$Cl$_2$ showed mass peaks assigned to Br(cpeb).

Table 1. Photochemical data of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption $^a$)</th>
<th>Emission $^b$)</th>
<th>Stokes shift $^d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>$\phi$</td>
</tr>
<tr>
<td>cpeb</td>
<td>319</td>
<td>403 (406)$^c$</td>
<td>0.15 (0.14)$^d$</td>
</tr>
<tr>
<td>cpeb+Cl$^+$</td>
<td>357</td>
<td>508 (406)$^c$</td>
<td>0.12 (&lt;0.01)$^d$</td>
</tr>
<tr>
<td>cpeb+Br$^-$</td>
<td>358</td>
<td>503 (406)$^c$</td>
<td>0.05 (&lt;0.01)$^d$</td>
</tr>
<tr>
<td>cpeb+Ag$^+$</td>
<td>332</td>
<td>501</td>
<td>0.03</td>
</tr>
<tr>
<td>cpeb+Pd$^{2+}$</td>
<td>330</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>cpeb+Zn$^{2+}$</td>
<td>332</td>
<td>504 (485)$^e$</td>
<td>0.09 (0.15)$^g$</td>
</tr>
<tr>
<td>cpeb+H$^+$</td>
<td>353</td>
<td>495 (495)$^e$</td>
<td>0.16 (0.19)$^f$</td>
</tr>
</tbody>
</table>

$^a$) [cpeb] = 1.0 x 10^-2 mM, CH$_2$Cl$_2$, 25 °C. $^b$) [cpeb] = 1.0 x 10^-3 mM, CH$_2$Cl$_2$, 25 °C, $\lambda_{\text{ex}}$ = $\lambda_{\text{max}}$(absorption). $^c$) Quantum yield. $^d$) Stokes shift, $\Delta\lambda = \lambda_{\text{max}}$(absorption) - $\lambda_{\text{max}}$(absorption). $^e$) data in solid state. $^f$) AgOTf (2 equiv to cpeb). $^g$) Pd(OCOCF$_3$)$_2$ (4 equiv to cpeb). $^h$) Zn(OTf)$_2$ (2 equiv to cpeb). $^i$) CF$_3$COOH (1.0 mM). $^j$) Br$^+$OTf (1 equiv to cpeb). $^k$) Cl$^+$OTf (1 equiv to cpeb).
NMR time scale. Probably due to a heavy atom effect. The mixture of cpeb with CD in the mixture of cpeb with AgOTf, Pd(OCOCF$_2$)$_2$ showed clearly separated signals (spectra of the mixture of cpeb and X (X = Cl, Br) in CD$_2$Cl$_2$ showed a broad signal at $\delta$ 7.5-8.0 while free cpeb showed clearly separated signals ($\delta$ 7.72 (C$_6$H$_5$N), 7.68 (C$_6$H$_4$), 7.53 (C$_6$H$_3$N), 7.43 (C$_6$H$_4$)). It suggests equilibration of the complex formation of cpeb and X’OTf (X = Cl, Br) on the NMR time scale.

Similar complexation and bathochromic shift are observed in the mixture of cpeb with AgOTf, Pd(OCOCF$_2$)$_2$, Zn(OTf)$_2$, and CF$_3$COOH (Table 1). The reaction of cpeb with Pd(OCOCF$_2$)$_2$ causes quenching of fluorescence in solution probably due to a heavy atom effect. The mixture of cpeb with Zn(OTf)$_2$ has similar emission both from the solution and from the solid state (in solution, $\lambda_{max}$ = 504 nm, $\varphi$ = 0.09; in solid state, $\lambda_{max}$ = 485 nm, $\varphi$ = 0.15 (absolute)). The complexation of CF$_3$COOH and cpeb requires large excess of CF$_3$COOH ([cpeb] = 1.0 $\times$ 10$^{-3}$ mM, [CF$_3$COOH] = 1.0 $\times$ 10$^{-1}$ mM) to reach a saturation point in emission, which indicates relatively lower ability of cpeb for complexation with H$^+$ than other cations described above. The complex of cpeb and CF$_3$COOH shows also emission both from the solution and from the solid state (in solution, $\lambda_{max}$ = 495 nm, $\varphi$ = 0.16; in solid state, $\lambda_{max}$ = 495 nm, $\varphi$ = 0.19 (absolute)).

Figure 3 illustrates the structure of a rhomboid-shaped cyclic pyridylethynyl benzene (cpeb) employed in this study and its plausible structures of the inclusion complexes. The smaller guest, such as Cl$^+$ and H$^+$, may form unsymmetric inclusion complex g(cpeb) in which guest prefers to unsymmetrical coordination by one donor atom. The guest molecule, such as Br$, Ag^+$, Pd$^{2+}$ and Zn$^{2+}$, whose size is similar to the cavity of the cpeb may form symmetric inclusion complex G(cpeb) (G = guest) in which the guest molecule (or ion) located at the midpoint of the nitrogen atom. Larger size ion such as I$^-$ may not be included due to the shape-persistence of cpeb.

Figure 4 shows the calculated energy potentials for the position of halonium in an N-X-N system in X(cpeb) (X = Cl$^+$, Br$^+$) using ORCA package (version 2.9.1). The diagram of Cl(cpeb) and of Br(cpeb) was calculated to have double-well and single-well potential system, respectively. The results indicate Cl$^+$ in an N-X-N system of Cl(cpeb) prefers the position close to one nitrogen than the other. Br$^+$ in Br(cpeb) system is located at the midpoint of N-X-N with similar interactions of Br$^+$ and the two nitrogen atoms. Erdélyi investigated the complexation of halonium and deuterated bis(2-pyridylethynyl)benzene by NMR spectroscopy as well as DFT calculation in which bromium cation is included at the midpoint of the nitrogen atoms of pyridyl groups. The optimization calculation for I$^-$(cpeb) did not converge well due to instability of the complex.

These results can be rationalized by the fitting of the halonium ions and the cavity of cpeb. N1-N1 distance of cpeb analyzed by X-ray crystallography is 4.30 Å which is shorter than corresponding N…N distance in bis(2,6-dimethylpyridyl)iononium dibromoiodate, [(IC$_6$H$_5$N$_2$2,6-Me$_2$)][BrBr] (N…N = 4.588 Å) and slightly longer than that in bis(quinoline)bromine perchlorate, [Br(quinoline)$_2$]ClO$_4$ (N…N = 4.285 Å) which indicate the N…N distance in cpeb is not long enough for inclusion of I$^-$ and proper for Br$^+$ inclusion. Relatively smaller Cl$^+$ tends to coordinate strongly to one nitrogen to from unsymmetric inclusion structure. Similar analysis by calculation for complex X(cpeb) (X = H, Zn, Ag) suggests the symmetric structure for large guest ions (Zn, Ag) and unsymmetric structure for relatively smaller ion (H) which is also explained by the size of the guest ions.

Figure 5 shows the calculated HOMO and LUMO of the ground state of Cl(cpeb) which has unsymmetric ground state with short distance between the Cl$^+$ and one nitrogen, as described above, LUMO orbital is localized from Cl$^+$ to phenylene units. Br(cpeb) was calculated to have symmetric ground state structure which has LUMO spreaded over the cpeb molecule.

Since the emission from symmetric structure (LUMO to HOMO) is derived from forbidden transition, the observed emission from Br$^+$ (cpeb) probably involves formation of unsymmetric transition state generated by intramolecular relaxation after excitation. Lower quantum yield of emission...
from Br(cpeb) (φ = 0.05) than that from Cl′(cpeb) (φ = 0.12) and relatively longer time of emission from Br(cpeb) (τ₀ = 10 ns) is ascribed to the large structural change from symmetric ground state structure of Br(cpeb) to the transition state with unsymmetric structure. The absorption shoulder peak at 400 nm observed in the mixture of cpeb and Cl′OTf is assigned to charge transfer (CT)-type absorption by TD-DFT (PBE38/TZVP) calculation suggesting the emission of X’(cpeb) (calculated to be 504 nm with oscillator strength f = 0.04 (for Cl) and 457 nm with f = 0.03 (for Br)) mainly consists of transition from HOMO to LUMO (calcd 285.9 nm), HOMO to LUMO (calcd 304.8 nm). The absorption shoulder peak at 359 nm mainly consists of transition to HOMO-1 to LUMO (calcd 285.9 nm), HOMO to LUMO (calcd 304.8 nm), and HOMO to LUMO+1 (calcd 340.4 nm, forbidden transition) respectively.

Conclusion

We synthesized a facile shape-persistent azamacroyclic molecule, cpeb, having two pyridyl units and observed its size selective inclusion of halonium ions, Cl’, Br’, and I’. Cl’ and Br’ form unsymmetric and symmetric inclusion complexes, respectively while I’ does not form an inclusion complex. The different types of inclusion of cpeb for halonium as well as Ag, Pd, Zn, and H, is ascribed to the matching and mismatching of the size of guest ions and the cavity of cpeb.

Experimental

General

1,2-Diethynylbenzene was prepared by literature methods. Other chemicals were commercially available. H and 13C{1H} NMR spectra were acquired on a Varian MERCURY-300 (300 MHz) and a Bruker AV-400M (400 MHz). Fast atom bombardment mass spectra (FABMS) and HR-ESI-TOF-MS were obtained from a JEOL JMS-700 (matrix, 2-nitrophenyl naphthyl ether (NPNOE)) and a microOTOF II (Bruker) spectrometers respectively. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. UV-visible absorption spectra were measured on a JASCO V-530 as 1.0 × 10⁻³ m solutions in CH₂Cl₂. Photoluminescence spectra were recorded as 1.0 × 10⁻³ M solutions in CH₂Cl₂. Quantum yields were estimated by comparison of the standard solution of quinine sulfate (1.0 M, φ = 0.546). The lifetime of the emission from the compounds was measured by the Time-Resolved Absorption and emission Spectra Analysis System (TRASA) in our institute equipped with Nd-YAG laser (λex = 355 nm, [compound] = 0.00001 mM, in CH₂Cl₂). Solid state photoluminescence spectra were recorded by absolute PL quantum yields measurement system (C9290-01, Hamamatsu Photonics K. K.) equipped with a Xe light source, monochromator, an integrating sphere, and a CCD spectrometer.

Synthesis of 1,2-bis(6-bromo-2-ethylpyridyl)benzene (2)

A THF solution (300 mL) of 2,6-dibromopyridine (19.0 g, 80 mmol), Et₃N (27.8 mL, 200 mmol) was degassed by freeze-pump-thaw cycles. To the solution, Cul (190 mg, 1.0 mmol), PdCl₂(PPh₃)₂ (702 mg, 1.0 mmol) and 1,2-diethylbenzene (2.52 g, 20 mmol) were successively added then the mixture was stirred for 48 h at 50 °C. After removal of solvent by evaporation, the organic products were dissolved in CH₂Cl₂ (300 mL), and the solution was washed with sat. NH₄Cl(aq) (100 mL). The separated organic phase was dried over MgSO₄, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 2/1, Rf = 0.65) to obtain 1,2-bis(6-bromo-2-ethylpyridyl)benzene (2) (4.01 g, 9.15 mmol, 46% yield) as yellow powder. Anal. Calcd for C₃₉H₂₇Br₂N₂: 54.83, H: 2.30, N: 6.39%.

Synthesis of C₃₉H₁₄Br₂(C≡C-H)=C≡C-PDMS (1)

THF/MeOH (100 mL/100 mL solution) containing C₃₉H₁₂-C≡C-TMS₂ (2.71 g, 10 mmol) and K₂CO₃ (6.9 g, 50 mmol) was stirred at room temperature for 12 h. The separated organic phase was washed with CH₂Cl₂ and extracted with CH₂Cl₂ and Ag, Pd, Zn, and H, was washed with water. The separated organic phase was dried over MgSO₄, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 1/1, Rf = 0.40) to obtain C₃₉H₁₂-C≡C(H)-C≡C-PDMS (2.31 g, 8.77 mmol, 87%).

Synthesis of 1-(6-[(3’-cyanopropyl)dimethylsilyl]acetyl)-2-ethynylpyridyl)-2-(6-bromo-2-ethylpyridyl)benzene (1)

THF solution (20 mL) of 2 (1.75 g, 4.0 mmol), Et₃N (40 mL, 290 mmol) was degassed by freeze-pump-thaw cycles. To the solution, Cul (38 mg, 0.20 mmol), PdCl₂(PPh₃)₂ (140 mg, 0.20 mmol) and C₃₉H₁₄-C≡C(H)-C≡C-PDMS (1.06 g, 4.0 mmol) were successively added then the mixture was stirred for 3 h. To the resulting solution CISMe₃{(CH₂)₄CN} (1.49 g, 11 mmol) was added at 0 °C, then the mixture was stirred for 24 h. The product was extracted with CH₂Cl₂ and washed with water. The separated organic phase was dried over MgSO₄, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 1/1, Rf = 0.40) yielded 1 (834 mg, 1.37 mmol, 34%) as a brown solid. H NMR (300 MHz, CDCl₃, r.t.) δ 7.91 (d, 1H, C₅H₅N, J = 8 Hz), 7.85 (d, 1H, C₅H₅N, J = 8 Hz), 7.79 (t, 1H, p-C₅H₅N, J = 8 Hz), 7.63-7.66 (m, 2H, C₆H₄), 7.58 (dd, 1H, C₅H₅N, J = 6, 3 Hz), 7.54 (t, 1H, p-C₅H₅N, J = 8 Hz), 7.49-7.53 (m, 3H, C₆H₄, C₅H₅N), 7.37-7.41 (m, 3H, C₆H₄, C₅H₅N), 7.34 (dd, 2H, C₆H₄, J = 6, 3 Hz), 2.34 (t, 2H, CH₂, J = 7 Hz), 1.73-1.83 (m, 2H, CH₂, C₅H₅N), 0.80 (m, 2H, CH₃), 0.23 (s, 6H, Me).

Synthesis of 1,2-bis(6-bromo-2-ethylpyridyl)benzene (2)

A THF solution (300 mL) of 2,6-dibromopyridine (19.0 g, 80 mmol), Et₃N (27.8 mL, 200 mmol) was degassed by freeze-pump-thaw cycles. To the solution, Cul (190 mg, 1.0 mmol), PdCl₂(PPh₃)₂ (702 mg, 1.0 mmol) and 1,2-diethylbenzene (2.52 g, 20 mmol) were successively added then the mixture was stirred for 48 h at 50 °C. After removal of solvent by evaporation, the organic products were dissolved in CH₂Cl₂ (300 mL), and the solution was washed with sat. NH₄Cl(aq) (100 mL). The separated organic phase was dried over MgSO₄, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 2/1, Rf = 0.65) to obtain 1,2-bis(6-bromo-2-ethylpyridyl)benzene (2) (4.01 g, 9.15 mmol, 46% yield) as yellow powder. Anal. Calcd for C₃₉H₂₇Br₂N₂: 54.83, H: 2.30, N: 6.39%.
Synthesis of cpeb

A THF/MeOH solution (THF/MeOH = 50 mL/50 mL) containing 1 (609 mg, 1.0 mmol) and K₂CO₃ (690 mg, 5.0 mmol) was stirred at room temperature for 12 h. After removal of the solvent by evaporation, the obtained organic product was dissolved in CH₂Cl₂ (300 mL) and the solution was washed with water (50 mL). The separated organic phase was dried over MgSO₄, filtered and evaporated to yield C₂H₃₋₁₋₄₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋₁₋₇₋₄₋₃₋₅₋₃₋₂₋₁₋₇₋₄₋₂₋�

Notes and references


21 \( \text{Pd(OCCF}_3\text{)}_2\text{(bpeb)} \) (bpeb = 1,2-bis(2-pyridylethynyl)benzene) was synthesized and the structure was analyzed by X-ray crystallography. See Supporting information.


24 The similar calculations were conducted by LPNO-CEPA/1, DFT(B3LYP, PBE38) and MP2. The result from PBE38 is similar to those from LPNO-CEPA/1 and LPNO-CCSD which are known as accurate theories of electron correlation. The results indicate the result from PBE38 possess higher reliability. B3LYP, employed in previous investigation for halonium-nitrogen coordination (ref 19), estimate also double-well potential curve with the smaller energy barrier in which the local minimums for N-Cl distances is shorter than those from LPNO-CEPA/1, LPNO-CCSD and PBE38. The result from MP2 calculation is different from those of the above methods, which has one local minimum.


28 S1 state of the exited state of Br+(cpeb) is calculated to have symmetric ground state structure.
A table of contents entry of

Rhomboid-shaped Organic Host Molecule with Small Binding Space. Unsymmetrical and Symmetrical Inclusion of Halonium Ions

Yuji Suzaki, Takashi Saito, Tomohito Ide and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology
4259 Nagastuta, Midori-ku, Yokohama 226-8503 (Japan)

A shape persistent rhomboid-shaped organic host molecule having two pyridyl unit was synthesized which induces the size selective halonium inclusion.