Dalton Transactions

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

Journal:	*Dalton Transactions*
Manuscript ID:	DT-ART-12-2013-053629.R1
Article Type:	Paper
Date Submitted by the Author:	02-Feb-2014
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Journal Name

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ARTICLE

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Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

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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^+, Pd^{2+}, Zn^{2+} and H^+, is also mentioned.

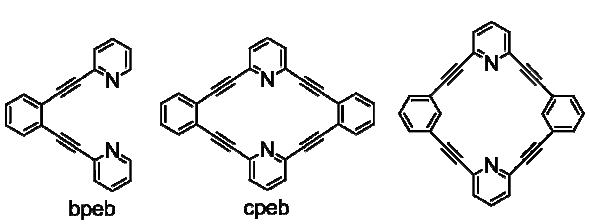
Introduction

The macrocyclic organic host molecules, such as crown ether[1], cryptand[2], calix arene[3], pillararene[4] and cyclodextrin[5], bind guest molecules as well as ions to form their inclusion complexes. Metal cations are complexed with the host molecules containing donor atoms or groups, such as dicyclohexano[18]crown-6-ether and [2.2.2]cryptand, $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$.[6,7] Inclusion of various metal ions and alkylammonium, was achieved by artificial design of the host molecules.[8] Halonium[9] is proposed as the intermediate of halogen addition reaction to alkene[10] and halolactamization[11] and contributes as a component of square-shaped dinuclear Pt complex.[12] Its isolation with aid of inclusion using cyclic host molecules has attracted much less attention than inclusion of the metal cations. Resnati reported halogen bonding in which donor atoms have significant interaction with halogen atom of the compound and recognition of guests based on it.[13] Recently, fluoronium "F^+" sources, such as *Selectfluor* (a derivative from DABCO), N-fluorobenzenesulfonimide (NFSI) and N-fluoro-2,4,6-trimethylpyridinium hexafluorophosphate, have gathered attention as electrophile in the electrophilic fluoronation of arenes catalyzed by Pd and Cu.[14,15] 1,2-Bis(2-pyridylethynyl)benzene (Scheme 1, bpeb), having two pyridyl groups tethered by a 1,2-dialkynyl benzene, function as a trans bidentate ligand of transition metal complexes[16,17] and the complexes of bromonium ion.[18,19]

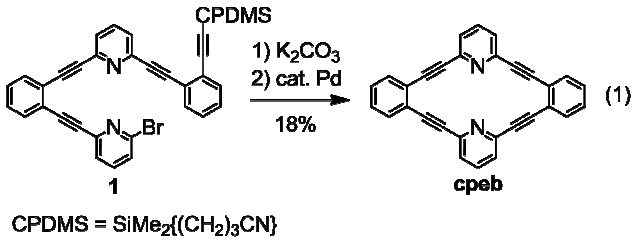
In this paper, we designed a cyclic organic host molecule composed of two pyridyl and two 1,2-dialkyl benzene units (cpeb) which is expected to have a similar N…N distance and a rigid structure, suited for complexation with haloniums. Here we report unique inclusion behavior of cpeb for the haloniums.

Results and discussion

Eq 1 depicts the synthesis of cyclic pyridylethynylbenzene (cpeb) by deprotection of -$SiMe_2\{(CH_2)_3CN\}$ group of **1** under basic condition followed by intramolecular Sonogashira-Hagihara cross-coupling reaction of **1**. The palladium(II) complex, $Pd(OCOCF_3)_2$(cpeb), was obtained by reaction of $Pd(OCOCF_3)_2$ and cpeb in 70%. Fig. 1 shows molecular structures of cpeb and its complex with $Pd(OCOCF_3)_2$ 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 $Pd(OCOCF_3)_2$(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.



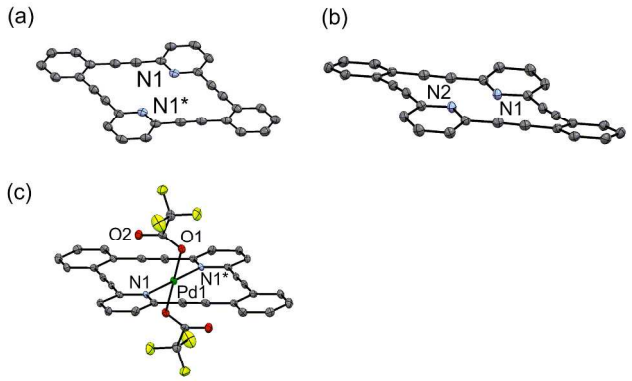


Fig. 1. Crystal structure of (a) cpeb (space group = *Cmce* (no.64)), (b) cpeb (space group = *Pbca* (no.61)) and (b) $Pd(OCOCF_3)_2$(cpeb)

Yoshida et al selected macrocyclic molecule, a cyclyne-type azamacrocycles having two pyridine units and two 1,3-dialkyl benzene as the host and found its light-emitting inclusion complex with $Sb(V)Cl_5$.[20] 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.[21,22]

UV-vis spectroscopy measurements revealed a remarkable bathochromic shift of cpeb (λ_{max} = 319 nm) upon addition of Cl^+OTf^- (λ_{max} = 357 nm) and Br^+OTf^- (λ_{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^-. The Job's plots of the absorption intensity at 410 nm of the mixture of cpeb and Br^+OTf^- ([cpeb] + [Br^+OTf^-] = 1.0 × 10^{-2} mM, CH_2Cl_2, 25 °C) shows a maximum at molar fraction close to 0.5, which indicates that cpeb and Br^+OTf^- form 1:1 complex in CH_2Cl_2 solution.

Emission spectra also show the bathochromic shifts upon complexation of Cl^+ and Br^+. Excitation of the mixture of cpeb and Cl^+OTf^- at λ_{ex} = 357 nm results in green emission (λ_{max} = 508 nm) with Stokes shift of 1.00 eV and moderate quantum yield (φ = 0.12), while cpeb shows emission at λ_{max} = 403 nm with smaller Stokes shift (0.81 eV) (Figure 2b). The quantum yield from Cl^+(cpeb) (φ = 0.12) is higher than that of Br^+(cpeb)

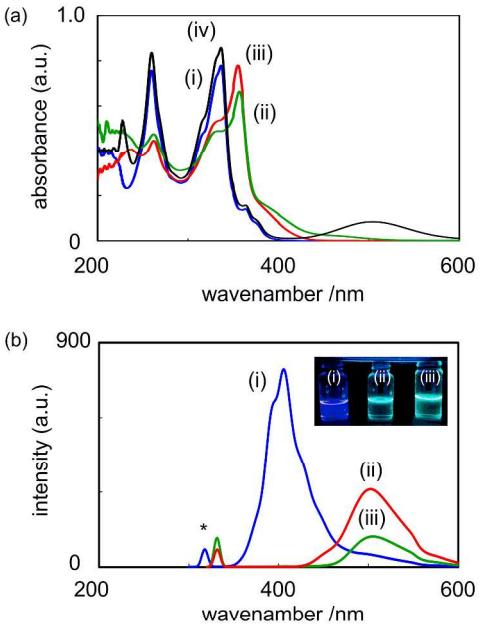


Figure 2. (a) absorption spectra of (i) cpeb (blue, [cpeb] = 1.0 × 10^{-2} mM), (ii) cpeb + Cl^+OTf^- (red, [Cl^+OTf^-] = 1.0 × 10^{-2} mM), (iii) cpeb + Br^+OTf^- (green, [Cl^+OTf^-] = 1.0 × 10^{-1} mM) and (iv) cpeb + I^+OTf^- (black, [I^+OTf^-] = 1.0 × 10^{-1} mM) and (b) emission spectra of (i) cpeb (blue, [cpeb] = 1.0 × 10^{-3} mM), (ii) cpeb + Cl^+OTf^- (red, [Cl^+OTf^-] = 1.0 × 10^{-3} mM), (iii) cpeb + Br^+OTf^- (green, [Cl^+OTf^-] = 1.0 × 10^{-3} mM). Photograph under irradiation at 365 nm is shown in the inset ((i) cpeb, (ii) cpeb + Cl^+OTf^-, (iii) cpeb + Br^+OTf^-)

(φ = 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, λ_{ex} = 365 nm). The lifetime of emission from the mixture of cpeb and Br^+OTf^- (τ_0 = 10 ns) is longer than that of cpeb (τ_0 = 6.5 ns). The solid-state emission from cpeb (λ_{max} = 403 nm, φ = 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 (φ < 0.01 (absolute)).

HR-ESI-MS spectra obtained from the mixture of cpeb and Br^+OTf^- in CH_2Cl_2 showed mass peaks assigned to Br(cpeb)

Table 1. Photochemical data of compounds

Compound	Absorption [a]	Emission [b]			Stokes shift /eV (/nm) [d]
	λ_{max} / nm	λ_{max} / nm	ϕ [c]	τ_0 /ns	
cpeb	319	403 (406)[e]	0.15 (0.14)[e]	6.5	0.81 (84)
cpeb+Cl^+ [k]	357	508 (-)[e]	0.12 (<0.01)[e]	-	1.00 (169)
cpeb+Br^+ [j]	358	503 (-)[e]	0.05 (<0.01)[e]	10	0.99 (171)
cpeb+Ag^+ [f]	332	501	0.03	-	1.25 (169)
cpeb+Pd^{2+} [g]	330	-	-	-	-
cpeb+Zn^{2+} [h]	332	504 (485)[e]	0.09 (0.15)[e]	5.7	1.27 (172)
cpeb+H^+ [i]	353	495 (495)[e]	0.16 (0.19)[e]	9.7	1.00 (113)

[a] [cpeb] = 1.0 × 10^{-2} mM, CH_2Cl_2, 25 °C. [b] [cpeb] = 1.0 × 10^{-3} mM, CH_2Cl_2, 25 °C, λ_{ex} = λ_{max}(absorption). [c] Quantum yield. [d] Stokes shift, $\Delta\lambda$ = λ_{max}(absorption) - λ_{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_3COOH (1.0 mM). [j] Br^+OTf^- (1 equiv to cpeb). [k] Cl^+OTf^- (1 equiv to cpeb).

(*m/z* = 483.029, calcd 483.032). HR-ESI-MS spectra of the mixture of cpeb and Cl^+OTf^- showed mass peaks at *m/z* = 509.0306 and 913.1505 which is assigned to the hydrochloric acid adduct of the complex, $Cl(cpeb)(HCl)_2$ (calcd 509.0346) and $Cl_3(cpeb)_2(HCl)_2$ (calcd 913.1532), respectively. ^1H NMR spectra of the mixture of cpeb and X^+OTf^- (X = Cl, Br) in CD_2Cl_2 showed a broad signal at δ 7.5-8.0 while free cpeb showed clearly separated signals (δ 7.72 (C_5H_3N), 7.68 (C_6H_4), 7.53 (C_5H_3N), 7.43 (C_6H_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, $Pd(OCOCF_3)_2$, $Zn(OTf)_2$ and CF_3COOH (Table 1). The reaction of cpeb with $Pd(OCOCF_3)_2$ causes quenching of fluorescence in solution probably due to a heavy atom effect. The mixture of cpeb with

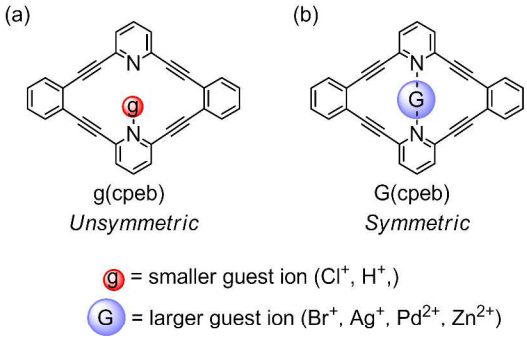


Fig. 3. Structure of inclusion complex of cpeb with (a) smaller (Cl^+, H^+) and (b) larger (Br^+, Ag^+, Pd^{2+}, Zn^{2+}) guest ions.

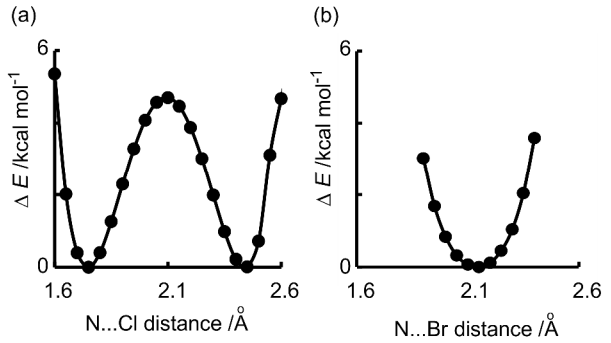


Fig. 4. Calculated potential energy curve and N(1)...X distance in N(1)...X...N(2) in (a) [Cl^+(cpeb)] and (b) [Br^+(cpeb)]. The energies for the model structures of (X)(cpeb) were calculated at every 0.05 Å distance of the rigid N(1)...X...N(2) unit (N(1)...N(2) = 4.19 Å) using the PBE38/TZVP basis set.

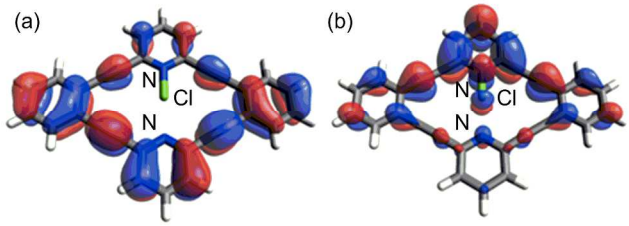


Fig. 5. The (a) HOMO and (b) LUMO of the ground state of Cl(cpeb) caluculated by DFT calculation (PBE38/TZVP).

$Zn(OTf)_2$ has similar emission both from the solution and from the solid state (in solution, λ_{max} = 504 nm, φ = 0.09; in solid state, λ_{max} = 485 nm, φ = 0.15 (absolute)). The complexation of CF_3COOH and cpeb requires large excess of CF_3COOH ([cpeb] = 1.0×10^{-3} mM, [CF_3COOH] = 1.0×10^{-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_3COOH shows also emission both from the solution and from the solid state (in solution, λ_{max} = 495 nm, φ = 0.16; in solid state, λ_{max} = 495 nm, φ = 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).[23] 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 bromiun cation is included at the midpoint of the nitrogen atoms of two pyridyl groups.[19] The optimization calculation for I^+(cpeb) did not converge well due to instability of the complex.[24]

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)iononinum dibromoiodate, $[I(C_5H_3N\text{-}2,6\text{-}Me_2)]^+[BrIBr]^-$ (N…N = 4.588 Å)[25] and slightly longer than that in bis(quinoline)bromine perchlorate, $[Br(quinoline)_2]ClO_4$, (N…N = 4.285 Å)[26,27] 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[28], 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 life time of emission from Br(cpeb) (τ_0 = 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. TD-DFT (PBE38/TZVP) calculation suggests that the absorption peaks of cpeb observed at 259, 318 and 340 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 azamacrocyclic 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[29] was prepared by literature methods. Other chemicals were commercially available. ^1H and $^{13}C\{^1H\}$ 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 *n*-octyl ether (NPOE)) and a micrOTOF 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^{-2} mM solutions in CH_2Cl_2. Photoluminescence spectra were recorded as 1.0×10^{-3} M solutions in CH_2Cl_2. 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 (λ_{ex} = 355 nm, [compound] = 0.00001 mM, in CH_2Cl_2). Solid state photoluminescence spectra were recorded by absolute PL quantum yields measurement system (C9920-01, 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-ethynylpyridyl)benzene (2)

A THF solution (300 mL) of 2,6-dibromopyridine (19.0 g, 80 mmol), Et_3N (27.8 mL, 200 mmol) was degassed by freeze-pump-thaw cycles. To the solution, CuI (190 mg, 1.0 mmol), $PdCl_2(PPh_3)_2$ (702 mg, 1.0 mmol) and 1,2-diethynylbenzene (2.52 g, 20 mmol) were successively added then the mixture was stirred for 48 h at 50 ^oC. After removal of solvent by evaporation, the organic products were dissolved in CH_2Cl_2 (300 mL), and the solution was washed with sat. NH_4Cl(aq) (100 mL). The separated organic phase was dried over $MgSO_4$, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 2/1, R_f = 0.65) to obtain 1,2-bis(6-bromo-2-ethynylpyridyl)benzene (**2**) (4.01 g, 9.15 mmol, 46%) as yellow powder. Anal. Calcd for $C_{20}H_{10}Br_2N_2$, C: 54.83, H: 2.30, N: 6.39%. Found, C: 54.99, H: 2.22, N: 6.26%. ^1H NMR (300 MHz, $CDCl_3$, r.t.) δ 7.85 (d, 2H, 3-C_5H_4N, J = 8 Hz), 7.64 (dd, 2H, *m*-C_6H_4, J = 6, 3 Hz), 7.63 (t, 2H, 4-C_5H_4N, J = 8 Hz), 7.47 (d, 2H, 5-C_5H_4N, J = 8 Hz), 7.40 (dd, 2H, *o*-C_6H_4, J = 6, 3 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, r.t.) δ 144.0, 141.8, 138.7, 132.3, 129.3, 127.7, 127.0, 125.6, 92.3 (C≡C), 89.2 (C≡C). HRMS (ESI-TOF-MS): Calcd for $C_{20}H_{11}Br_2N_2$ 438.9383; found, m/z 438.9253 $[M+H^+]^+$.

Synthesis of C_6H_4-1,2-(C≡C-H)(C≡C-CPDMS)

THF/MeOH (100 mL/100 mL) solution containing C_6H_4-1,2-(C≡C-TMS)$_2$ (2.71 g, 10 mmol) and K_2CO_3 (6.9 g, 50 mmol) was stirred at room temperature for 12 h. The separated organic phase was dried over $MgSO_4$ and evaporated to yield C_6H_4-1,2-(C≡C-H)$_2$ which was dissolved in dry THF (80 mL). To the solution, EtMgBr (1M solution in THF, 10 mL, 10 mmol) was added at 0 ^oC, then the mixture was stirred for 3 h. To the resulting solution $ClSiMe_2\{(CH_2)_3CN\}$ (1.49 g, 11 mmol) was added at room temperature, then the mixture was stirred for 24 h. The product was extracted with CH_2Cl_2 and washed with water. The separated organic phase was dried over $MgSO_4$, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 1/1, R_f = 0.4) to obtain C_6H_4-1,2-(C≡C-H)(C≡C-CPDMS) (2.31 g, 8.7 mmol, 87%) as colorless oil. ^1H NMR (300 MHz, $CDCl_3$, r.t.) δ 7.51-7.45 (m, 2H), 7.32-7.27 (m, 2H), 3.33 (s, 1H, ≡C-H), 2.44 (t, 2H, CH_2CN, J = 6.8 Hz), 0.86 (m, 2H, CH_2), 0.27 (s, 6H, Me).

Synthesis of 1-(6-[{(3'-cyanopropyl)dimethylsilyl}acetyl]-2-ethynylpyridyl)-2-(6-bromo-2-ethynylpyridyl)benzene (1)

THF solution (20 mL) of **2** (1.75 g, 4.0 mmol), Et_3N (40 mL, 290 mmol) was degassed by freeze-pump-thaw cycles. To the solution, CuI (38 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol) and C_6H_4-1,2-(C≡C-H)(C≡C-CPDMS) (1.06 g, 4.0 mmol) were successively added, then the mixture was stirred for 36 h at 50 ^oC. The resulting mixture was concentrated by evaporation. The obtained organic product was dissolved in CH_2Cl_2 (300 mL) and the solution was washed with sat. NH_4Cl(aq) (100 mL). The separated organic phase was dried over $MgSO_4$, filtered and evaporated to form a crude product as yellow oil. Purification by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 2/1, R_f = 0.40) yielded **1** (834 mg, 1.37 mmol, 34%) as a brown solid. ^1H NMR (300 MHz, $CDCl_3$, r.t.) δ 7.91 (d, 1H, C_5H_4N, J = 8 Hz), 7.85 (d, 1H, C_5H_4N, J = 8 Hz), 7.79 (t, 1H, *p*-C_5H_4N, J = 8 Hz), 7.63-7.66 (m, 2H, C_6H_4), 7.58 (dd, 1H, C_6H_4, J = 6, 3 Hz), 7.54 (t, 1H, *p*-C_5H_4N, J = 8 Hz), 7.49-7.53 (m, 2H, C_6H_4, C_5H_4N), 7.37-7.41 (m, 3H, C_6H_4, C_5H_4N), 7.34 (dd, 2H, C_6H_4, J = 6, 3 Hz), 2.34 (t, 2H, CH_2, J = 7 Hz), 1.73-1.83 (m, 2H, CH_2, C_5H_4N), 0.80 (m, 2H, CH_2), 0.23 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$, r.t.) δ 144.0, 143.9, 143.7, 141.8, 138.8, 136.8, 132.6, 132.5, 132.2, 132.2, 129.3, 129.1, 129.0, 128.7, 127.7, 127.4, 127.2, 126.7, 125.9, 125.8, 125.5, 125.1, 119.9 (CN), 104.5 (C≡C), 97.4 (C≡C), 93.1 (C≡C), 92.3 (C≡C), 92.2 (C≡C), 89.3 (C≡C), 88.1 (C≡C), 88.0 (C≡C), 20.8 (CH_2), 20.6 (CH_2), 15.7 (CH_2), -1.7 (Me). Anal. Calcd for $C_{36}H_{26}BrN_3Si$, C: 71.05, H: 4.31, Br: 13.13, N: 6.90%. Found, C: 70.33, H: 4.24, Br: 12.71, N: 6.60%. HRMS (ESI-TOF-MS): Calcd for $C_{36}H_{26}BrN_3Si$+Na: 630.0977, Found: m/z = 630.0970 $[M+Na^+]$

Synthesis of cpeb

A THF/MeOH solution (THF/MeOH = 50 mL/50 mL) containing **1** (609 mg, 1.0 mmol) and K_2CO_3 (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 CH_2Cl_2 (300 mL) and the solution was washed with water (50 mL). The separated organic phase was dried over $MgSO_4$, filtered and evaporated to yield C_6H_4-1-(C≡C-C_6H_3N-6-C≡C-C_6H_4-2-C≡CH)-2-(C≡C-C_6H_3N-Br) as yellow oil. The above product was dissolved in THF/Et_3N (100 mL/100 mL), and the solution was degassed by freeze-pump-thaw cycles. To the mixture, CuI (9.5 mg, 0.05 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.005 mmol) was successively added, and the solution was stirred at 50 °C for 48 h. The resulting mixture was concentrated by evaporation. The obtained organic product was dissolved in CH_2Cl_2 (200 mL) and the solution was washed with sat NH_4Cl(aq) (100 mL). The separated organic phase was dried over $MgSO_4$, filtered and evaporated to yield crude product as black solid. Purification by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 2/1, R_f = 0.40) yielded cpeb (834 mg, 1.37 mmol, 34%) as brown powder. ^{1}H NMR (400 MHz, CD_2Cl_2, r.t.) δ 7.34 (dd, 4H, *o*-C_6H_4, *J* = 6, 3 Hz), 7.44 (d, 4H, 3-C_5H_4N, *J* = 8 Hz), 7.59 (dd, 4H, *m*-C_6H_4, *J* = 6, 3 Hz), 7.63 (t, 2H, 4-C_5H_4N, *J* = 8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, r.t.) δ 144.3 (2-C_5H_4N), 136.8 (4-C_5H_4N), 133.1 (*o*-C_6H_4), 129.5 (*m*-C_6H_4), 126.9 (3-C_5H_4N), 125.9 (*ipso*-C_6H_4), 93.3 (C≡C), 87.6 (C≡C). HRMS (ESI-TOF-MS): Calcd for $C_{30}H_{14}N_2$+Na: 425.1055, Found: *m/z* = 425.1049 [M+Na^+].

Synthesis of $Pd(OCOCF_3)_2$(cpeb)

A CH_2Cl_2 solution of cpeb (50 mM, 10 mL, 5 μmol) was added to the THF solution of CF_3COOH (5.0 mM, 1.2 mL, 6.0 μmol), and the mixture was stirred at 50 °C for 12 h. Separated brown solid of $Pd(OCOCF_3)_2$(cpeb) was collected by filtration (2.6 mg, 3.5 μmol, 70%). HRMS (ESI-TOF-MS): Calcd for $C_{30}H_{14}N_2Pd$: 508.0182, Found: *m/z* = 508.0213 [M-2$(OCOCF_3)_2$]$^+$. Low solubility of the compound prevented NMR measurement. Similar reaction in $CDCl_3$ without stirring yielded $Pd(OCOCF_3)_2$(cpeb) as single crystals which are subjected to X-ray structure analyses.

X-ray structure analyses

Crystals of cpeb and $Pd(OCOCF_3)_2$(cpeb) suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2 (cpeb (*Cmce* (no. 64)), CH_2Cl_2/HCl(aq) (cpeb (*Pbca* (no. 61)) and $CDCl_3$ ($Pd(OCOCF_3)_2$(cpeb)). All measurements were made on Rigaku AFC-10R Saturn or Bruker ApexII CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were carried out by using a program package Crystal Structure™ for Windows.[30] All hydrogen atoms were included at the calculated positions with fixed thermal parameters

Acknowledgements

We thank our colleagues in the Chemical Resources Laboratory of Tokyo Institute of Technology for their technical support and discussions; Dr. Yoshihisa Sei for X-ray crystallography and life-time measurement in the Center for Advanced Materials Analysis of our institute. Dr. Takanori Fukushima and Dr. Yoshiaki Shoji for measurement of emission spectra (solid state). This work was supported by Grant-Aid for Scientific Research for Young Scientists from the Ministry of Education, Culture, Sports, Science and Technology, Japan (25810059), and for Scientific Research on Innovative Areas "Coordination Program" (24108711).

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† Electronic Supplementary Information (ESI) available: additional figures, UV and NMR spectra as well as theoretical calculation. CCDC 973075, 973076 and 973077. For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x/

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A table of contents entry of

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

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