The first two examples of halogen bonding with a sigma hole-donating fluorine in $\mathrm{C}_{\mathrm{sp} 3}-\mathrm{F} \cdots \mathrm{O}_{\mathrm{sp} 3}$ interaction from poly-fluorinated trans-dihalo-palladium(II) disubstituted pyridine complexes

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Electronic Supplementary Information (ESI)

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## Experimental Sections

General procedures. Gas chromatographic/mass spectrometric data were obtained using an Agilent 6890 Series gas chromatograph with a series 5973 mass selective detector. Reactions were monitored with a HP 6890 GC using a 30 m 0.250 mm HP-1 capillary column with a 0.25 mm stationary phase film thickness. The flow rate was $1 \mathrm{~mL} / \mathrm{min}$ and split-less. Samples analyzed by fast atom bombardment (FAB) mass spectroscopy were carried out by staff of the National Central University (Taiwan) mass spectrometry laboratory. Infrared spectra were obtained on a Perkin Elmer RX I FT-IR spectrometer. NMR spectra were recorded on Bruker AM 500 and 300 spectrometers using $5-\mathrm{mm}$ o.d. sample tubes. $\mathrm{CD}_{3} \mathrm{OD}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \mathrm{CDCl}_{3}$, deuterated DMF, and deuterated DMSO were the references for both ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra, while Freon ${ }^{\circledR} 11\left(\mathrm{CFCl}_{3}\right)$ was the reference for ${ }^{19} \mathrm{~F}$ NMR spectra. Table S2 lists part of the parameters in X-ray studies employing a Bruker single-crystal diffractometer equipped with a CCD area detector and graphite-monochromatized Mo $\mathrm{K} \alpha$ radiation ( $\lambda 0.71073 \AA$ ). Chemicals, reagents, and solvents employed were commercially available and used as received.

## Computational method for vibrational study

Theoretical calculations were performed using the Gaussian 16 packages. ${ }^{1}$ For the geometry optimizations, the crystal geometries of two ligand molecules with interactions shown in Fig. 1a were taken for calculations and performed using the APFD DFT functional with a basis set of def2-SVP for all the atoms. The vibrational frequency analysis of the corresponding dimers were carried out while the optimized structure represented the local energy minimum.

Synthesis of 3-[(2,2,3,3-tetrafluoropropoxy)methyl]pyridine ${ }^{2}$ : 2,2,3,3-Tetrafluoropropan-1-ol ( 0.83 g , 6.3 mmol ) and $30 \% \mathrm{CH}_{3} \mathrm{ONa} / \mathrm{CH}_{3} \mathrm{OH}(5.1 \mathrm{mmol})$ were mixed in a double-necked flask and continuously stirred at 333 K under nitrogen for 4 hours. The methanol was removed using a vacuum system to shift the reaction to the product side. The obtained sodium fluorinated alkoxide was dissolved in dry THF (20 mL ), and then $3-\mathrm{BrCH}_{2}$-pyridine ( $0.67 \mathrm{~g}, 3.9 \mathrm{mmol}$ ) was added, and the mixture was continuously stirred for 4 hours under a nitrogen atmosphere at 333 K . The resulting solution was extracted with dichloromethane and water to give 3-[(2,2,3,3-tetrafluoropropoxy)methyl]pyridine as a pale yellow liquid, and then a distillation system was applied to remove excess solvent to obtain pure $3-[(2,2,3,3-$ tetrafluoropropoxy)methyl]pyridine, which is the transparent liquid.

Synthesis of complex (1): 3-[(2,2,3,3-tetrafluoropropoxy)- methyl]pyridine ( $1.74 \mathrm{~g}, 7.8 \mathrm{mmol}$ ) was mixed with K 2 PdCl 4 using dry DMSO in a round bottom flask and at 333 K under nitrogen for 4 hours. Then a distillation system was used to remove excess solvent to obtain a crude product. The crude product was dissolved in ethanol ( 10 mL ), and then water was added ( 200 mL ) to precipitate it out. After suction filtration, white powder was obtained. The yield of the white product (1) ( $833 \mathrm{mg}, 1.2 \mathrm{mmol}$ ) was $92 \%$.

Synthesis of complex (2): In the case of bromide complex, similar synthesis procedure was followed using $\mathrm{K}_{2} \mathrm{PdBr}_{2}$ to obtain a pale yellow powder. The yield of $\mathbf{t}-\left[(\mathbf{3} \mathbf{- 4 F H} \mathbf{- p y})_{2} \mathbf{P d B r}_{2}\right](812 \mathrm{mg}, 1.0 \mathrm{mmol})$ was $77 \%$.

## Analytical data of $\left.\mathbf{t - [ ( 3 - 4 F H - p y )} \mathbf{2 P d C l}_{2}\right](\mathbf{1})$

m.p. $138{ }^{\circ} \mathrm{C},{ }^{1} \mathrm{H}-\mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm})=8.77\left(2 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.0 \mathrm{~Hz}, \mathrm{H}_{6}\right), 8.77(2 \mathrm{H}, \mathrm{s}$, $\left.\mathrm{H}_{2}\right), 7.77\left(2 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{H}_{4}\right), 7.35\left(2 \mathrm{H}, \mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=5.8 \mathrm{~Hz}, \mathrm{H}_{5}\right), 5.93(2 \mathrm{H}, \mathrm{tt}$, ${ }^{2} \mathrm{~J}_{\mathrm{HF}}=53.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HF}}=5.0 \mathrm{~Hz}$, terminal H$), 4.65\left(4 \mathrm{H}, \mathrm{s}\right.$, py $\left.-\mathbf{C H}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}, \mathrm{H} 7\right), 3.91(4 \mathrm{H}, \mathrm{tt}$, ${ }^{3} \mathrm{~J}_{\mathrm{HF}}=13 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HF}}=2.0 \mathrm{~Hz}$, py- $\left.\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}, \quad \mathrm{H} 8\right) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$, $\delta(\mathrm{ppm})=152.9, \quad 152.0, \quad 137.6, \quad 134.5, \quad 124.8, \quad(10 \mathrm{C}, \mathrm{s}, \mathrm{py}), 117.0 \sim 106.9$, (4C, ру$\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ) 70.7, (2C, s, py- $\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ) 67.7 , ( $2 \mathrm{C},{ }^{3} \mathrm{~J}_{\mathrm{CF}}=27.88 \mathrm{~Hz}$, py$\left.\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right) ;{ }^{19} \mathrm{~F}-\mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm})=-124.37$, (4F, s, py$\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ) -138.90, (4F, s, py- $\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ). FT-IR: $v\left(\mathrm{~cm}^{-1}\right)=1614,1587$, 1471, 1447 (vpy, m), 1135, 1092 (C-F, stretch); HR-FAB [(M-Cl) $\left.{ }^{+} ; \mathrm{m} / \mathrm{z}=\right] \mathrm{C}_{18} \mathrm{H}_{18}{ }^{35} \mathrm{ClF}_{8} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}$ calcd $\mathrm{m} / \mathrm{z} 586.9964$, found $586.9962 \mathrm{C}_{18} \mathrm{H}_{18}{ }^{37} \mathrm{ClF}_{8} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}$ calcd m$/ \mathrm{z} 588.9968$, found 588.9936.

## Analytical data of $\left.\mathbf{t}[\mathbf{( 3 - 4 F H}-\mathbf{p y})_{2} \mathbf{P d B r}_{2}\right](2)$ :

m.p. $=141{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}-\mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm})=8.82\left(2 \mathrm{H}, \mathrm{s}, \mathrm{H}_{2}\right) 8.79\left(2 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=5.5 \mathrm{~Hz}, \mathrm{H}_{6}\right)$, $7.75\left(2 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{H}_{4}\right), 7.34\left(2 \mathrm{H}, \mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.0 \mathrm{~Hz}, \mathrm{H}_{5}\right), 5.93\left(2 \mathrm{H}, \mathrm{tt},{ }^{2} \mathrm{~J}_{\mathrm{HF}}=53.5 \mathrm{~Hz}\right.$, ${ }^{3} \mathrm{~J}_{\mathrm{HF}}=5.0 \mathrm{~Hz}$, terminal H$), 4.65\left(4 \mathrm{H}\right.$, s, py $\left.-\mathbf{C H}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right), 3.92\left(4 \mathrm{H}, \mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{HF}}=12 \mathrm{~Hz}\right.$, py$\left.\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right) ;{ }^{13} \mathrm{C}-\mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm})=153.9,152.9,137.4,134.5,124.9,(10 \mathrm{C}, \mathrm{s}$, py), $117.0 \sim 106.9$, (4C, py- $\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ) 70.6, (2C, s, py- $\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ) 67.7, ( $2 \mathrm{C},{ }^{3} \mathrm{~J}_{\mathrm{CF}}=27.9$ Hz , py- $\left.\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right) ;{ }^{19} \mathrm{~F}-\mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right), \delta(\mathrm{ppm})=-124.36$ (4F, s, py$\mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}$ ), -138.87 (4F, s, py-CH2OCH2CF2CF2H); FT-IR: $v\left(\mathrm{~cm}^{-1}\right)=1613,1586,1472,1446$ (vpy, m), 11361094 (C-F, stretch); $\mathrm{FAB}\left(\mathrm{M}+; \mathrm{m} / \mathrm{z}=\right.$ ) $\mathrm{C}_{18} \mathrm{H}_{18}{ }^{79} \mathrm{Br}_{2} \mathrm{~F}_{8} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}$ calcd m/z 709.8642, found 709.8632; $\mathrm{C}_{18} \mathrm{H}_{18}{ }^{81} \mathrm{Br}_{2} \mathrm{~F}_{8} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}$ calcd $\mathrm{m} / \mathrm{z} 713.8626$, found 713.8585; $\mathrm{C}_{18} \mathrm{H}_{18}{ }^{79} \mathrm{Br}^{81} \mathrm{Br}_{8} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}$ calcd $\mathrm{m} / \mathrm{z} 711.8622$, found 711.8620 .

Deuterated $\left.\mathbf{t - [ ( 3 - 4 F H - p y})_{2} \mathbf{P d C l}_{2}\right]$ : the deuterated compound of $\left.\left.\mathbf{t - [ ( 3 - 4 F H - p y}\right)_{2} \mathbf{P d C l}_{2}\right]$ is was also similarly prepared.
Some analytical data are shown below:
${ }^{1} \mathrm{H}-\mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})=8.86\left(1 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=5.5 \mathrm{~Hz}, \mathrm{H}_{6}\right), 8.84\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{2}\right), 7.78\left(1 \mathrm{H}, \mathrm{d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $\left.8.1 \mathrm{~Hz}, \mathrm{H}_{4}\right), 7.33\left(1 \mathrm{H}, \mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{H}_{5}\right), 5.93\left(1 \mathrm{H}, \mathrm{tt},{ }^{2} \mathrm{~J}_{\mathrm{FH}}=52.8,{ }^{3} \mathrm{~J}_{\mathrm{FH}}=4.5 \mathrm{~Hz},-\mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right), 3.92$ $\left(2 \mathrm{H}, \mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{FH}}=12.3 \mathrm{~Hz},-\mathrm{OCH}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{H}\right)$; FT-IR: $\mathrm{v}\left(\mathrm{cm}^{-1}\right)=2932,2889,2780\left(\mathrm{HC}_{2} \mathrm{~F}_{4}-\mathrm{CH}_{2}-\mathrm{O}-\mathrm{CD}_{2}\right.$ stretch $)$, 2184, 2164, $2078\left(\mathrm{CH}_{2}-\mathrm{O}-\mathrm{CD}_{2}\right.$ stretch ), 1614, 1587, 1471, 1447 (vpy, m), 1136, 1092 (C-F, stretch).

## Crystallization:

The samples of $\left.\mathbf{t - [ ( 3 - 4 F H - p y )} \mathbf{2}_{\mathbf{2}} \mathbf{P d C l}_{\mathbf{2}}\right]$ and $\mathbf{t}-\left[(\mathbf{3}-\mathbf{4 F H}-\mathbf{p y})_{\mathbf{2}} \mathbf{P d B r}_{2}\right]$ ( 30 mg ) were dissolved in dry DMF (2 mL ), and its top was layered with about water (about 3 mL ). After approximately 2 weeks of diffusion crystallization, the resulted single crystal was suitable for X-ray crystallographic studies.


Scheme S1. The schematic drawing of $t-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdX}_{2}\right]$ where $\mathrm{X}=\mathrm{Cl}, \mathrm{Br}$ with the labeling.

## 1. Molecular packing



Figure S1. Molecular packing diagrams of $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdBr}_{2}\right](2)$ (a) showing $\mathrm{C} 8 *-\mathrm{F} 2 * \cdots \mathrm{O} 1$ halogen bond (in green dash) and two weak interactions involving C8*-F2*F4-C9 (in orange dash) and tetrel bonding (in blue dash); (b) its stacking piles arranged in the herringbone pattern. [Note: C, O, $\mathrm{N}, \mathrm{F}, \mathrm{Br}$ and Pd are in grey, red, blue, yellow, brown and dark green color, respectively.]. The $\mathrm{r}\left(\mathrm{C} 8^{*}-\mathrm{F} 2 * \cdots \mathrm{O} 1\right), \mathrm{r}(\mathrm{F} 2 * \cdots \mathrm{~F} 4)$ and $\mathrm{r}(\mathrm{F} 2 * \cdots \mathrm{C} 6)$ are $2.839(2), 2.817$ and $3.094 \AA$, respectively. Furthermore, C8* and F2* are at an equivalent position ( $0.5+\mathrm{x}, 1.5-\mathrm{y}, 0.5+\mathrm{z}$ ).]

## 2. FT-IR spectra I



Figure S2.1. Experimental FT-IR spectra of (X) solid t-[(3-4FH-py) $\left.{ }_{2} \mathrm{PdBr}_{2}\right]$, and $(\mathrm{Y}) \mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdBr}_{2}\right]$ dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$; both show the $\mathrm{CH}_{2}$ vibrational stretches and their shifts. [Note: A description of the shifting of $\mathrm{CH}_{2}$ groups: when comparing the IR spectrum in solid state (trace $\mathrm{X},-$ ) with that in dbenzene solution (trace Y , -), the asymmetric and symmetric $\mathrm{CH}_{2}$ stretches have red shifted from 2980, 2934 and 2831 to 2916, 2886 and $2769 \mathrm{~cm}^{-1}$, respectively.

## 3. FT-IR spectra II



Figure S2.2. FT-IR spectra of solid t-[(3-4FH-py-d $\left.\left.)_{2}\right)_{2} \mathrm{PdCl}_{2}\right]$ (trace X-) and t-[(3-4FH-py-d $\left.)_{2} \mathrm{PdCl}_{2}\right]$ dissolved in benzene (trace $\mathrm{Y}-$ ) showing the asymmetric and symmetric stretches of $\mathrm{CD}_{2}$ group ${ }^{2}$. Note: When comparing the IR spectrum in solid state (trace X) with that in benzene solution (trace Y), the asymmetric and symmetric $\mathrm{CD}_{2}$ stretches are red-shifted from 2198, 2175 and 2092 to 2184, 2164 and $2078 \mathrm{~cm}^{-1}$, respectively.

## 4. Vibrational table

Table S1. The FT-IR studies of $\mathrm{CH}_{2}\left(\right.$ or $\left.\mathrm{CD}_{2}\right)$ stretches of solid and dissolved $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdCl}_{2}\right]$ and its solid deuterated species.

|  |  | $\mathbf{t}-\left[(\mathbf{3 - 4 F H - p y})_{2} \mathbf{P d C l}_{2}\right]$ <br> solid | $\mathbf{t}-\left[(\mathbf{3}-\mathbf{4 F H}-\mathbf{p y})_{2} \mathbf{P d C l}_{2}\right]$ <br> in benzene | deuterated <br> t-[(3-4FH-py $\left.)_{2} \mathbf{P d C l}_{2}\right]$ <br> solid |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{CH}_{2}$ Stretching frequencies $\left(\mathrm{cm}^{-1}\right)$ |  |

Note: ${ }^{i} \mathrm{NA}=$ not available. (and the stretches of $\mathrm{CD}_{2}$ group appear at 2184, 2164 and $2078 \mathrm{~cm}^{-1}$ shown in Fig. S.2.2.). t-[(3-4FH-py $\left.)_{2} \mathrm{PdCl}_{2}\right]=$ trans- $\left[\mathrm{PdCl}_{2}\left(3-\mathrm{HCF}_{2} \mathrm{CF}_{2} \mathrm{CH}_{2} \mathrm{OCD}_{2} \text { рy }\right)_{2}\right]$.

## 5. Computation section

The DFT functional have been used for calculations. The IR comparison table of $\mathrm{CH}_{2}$ groups are shown in Table S2 below. The numbers marked in yellow (both EXP and factored) represent the $\mathrm{CH}_{2}$ group whose stretches are influenced by C-F $\cdots \mathrm{O}$ and tetrel bond interactions. The numbers marked in green (EXP) represent the $\mathrm{CH}_{2}$ groups without intermolecular $\mathrm{C}-\mathrm{F} \cdots \mathrm{O}$ and tetrel bond interactions because the complex is dissolved in benzene. The numbers marked in pink (factored) represent the $\mathrm{CH}_{2}$ groups without intermolecular C-F $\cdots \mathrm{O}$ and tetrel bond interactions because this $\mathrm{CH}_{2}$ has not affected by C$\mathrm{F} \cdots \mathrm{O}$ and tetrel bond intermolecular interactions. Clearly, from the calculated results, the respective symmetric and two asymmetric stretches of $\mathrm{CH}_{2}$ group (next to py ring) which is affected by C-F $\cdots \mathrm{O}$ and tetrel bond interactions are $2829,2888,2910 \mathrm{~cm}^{-1}$. The respective symmetric and two asymmetric stretches of $\mathrm{CH}_{2}$ group (next to py ring) which have no $\mathrm{C}-\mathrm{F} \cdots \mathrm{O}$ and tetrel bond interactions are 2863, 2934, $2948 \mathrm{~cm}^{-1}$. Thus, based on theoretical calculations, the symmetric and asymmetric $\mathrm{CH}_{2}$ stretches have red shifted from 2863, 2934 and 2948 to 2829,2888 , and $2910 \mathrm{~cm}^{-1}$, respectively. In other words, the red shifting of $\mathrm{CH}_{2}$ group (next to py ring) has been confirmed by DFT calculations.

Table S2. The IR CH ${ }_{2}$ stretch comparison from both experiment and DFT calculations

| item | EXP | factored* <br> (factor=0.95) | unfactor |  |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 2770 | 2829 | 2978.3 | Symmetric $\mathrm{CH}_{2}$ stretch with intermolecular interaction |
| 2 | $\begin{array}{\|l} \hline(2830) \\ \text { (in } \left.\mathrm{C}_{6} \mathrm{H}_{6}\right) \\ \hline \end{array}$ | 2863 | 3013.3 | Symmetric $\mathrm{CH}_{2}$ stretch w/o interaction. |
| 3 | 2889 | 2888 | 3040.1 | asymmetric $\mathrm{CH}_{2}$ stretch with intermolecular interaction |
| 4 | 2917 | 2910 | 3062.7 | asymmetric $\mathrm{CH}_{2}$ stretch with intermolecular interaction |
| 5 | $\begin{aligned} & \hline(2931) \\ & \left(\text { in } \mathrm{C}_{6} \mathrm{H}_{6}\right) \\ & \hline \end{aligned}$ | 2934 | 3088.6 | asymmetric $\mathrm{CH}_{2}$ stretch w/o interaction. |
| 6 | $\begin{aligned} & \hline(2978) \\ & \left(\text { in } \mathrm{C}_{6} \mathrm{H}_{6}\right) \\ & \hline \end{aligned}$ | 2948 | 3103.0 | asymmetric $\mathrm{CH}_{2}$ stretch w/o interaction. |

Note: 1. The two fluorous pyridine ligands, which have the C-F $\cdots$ O bond, C-F $\cdots$ F-C interaction and tetrel bond shown in Fig. 1a, have been used for this DFT calculations. The stretch of pyridyl $\mathrm{CH}_{2}$ group from the left pyridine molecule (in Fig. 1a) which serves as F-atom donor is considered as the free $\mathrm{CH}_{2}$ group. Thus, their calculated $\mathrm{CH}_{2}$ stretches (next to py) are similar to those from the complex-dissolved benzene solution.
2. w/o: without; EXP: experiment.

## 6. Crystal packing



Figure S3.1. (a) Single molecule of trans-dichloro-palladium(II) bis(pyridine) complex; (b) Parallel arrangement of the molecules in the crystal packing.


Figure S3.2. (a) Single molecule of trans-dibromo-palladium(II) bis(pyridine) complex, trans-[ $\left.\mathrm{PdBr}_{2}(\mathrm{py})_{2}\right]$; (b) Parallel arrangement of the molecules in the crystal packing (without formation of the herringbone type of packing). ${ }^{3}$

## 7. Hirshfeld surface analysis



Figure S4.1. Hirshfeld surface ${ }^{4}$ analysis mapped with $\mathrm{d}_{\text {norm }}$ for $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdBr}_{2}\right](\mathbf{2})$ (a) Hirshfeld surface of single molecule and the main interactions formed in the herringbone structure. Three interactions are marked inside the red circle, $\mathrm{C}_{\mathrm{sp} 3}-\mathrm{F}^{\cdots} \mathrm{O}_{\mathrm{sp} 3}$ interaction pointed by a yellow arrow; (b) (enlarged image of S4a) Intermolecular interactions indicated with connecting lines between two related atoms.

## 8. Hirshfeld surface analysis of $d_{i}$ and $d_{e}$ of $t-\left[(3-4 F H-p y)_{2} \mathrm{PdCl}_{2}\right]$


(a) $\mathrm{d}_{\mathrm{i}}$

(b) $\mathrm{d}_{\mathrm{e}}$

Figure S 4.2 . The $\mathrm{d}_{\mathrm{i}}(\mathrm{S} 4.2 \mathrm{a})$ and $\mathrm{d}_{\mathrm{e}}(\mathrm{S} 4.2 \mathrm{~b})$ Hirshfeld surface of $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py}){ }_{2} \mathrm{PdCl}_{2}\right]$; for the $\mathrm{d}_{\mathrm{i}}$ mapping (Fig. S4.2a), the red spots pointed by arrows show the distance of atom (C6, O1 or F4) to the surface less than the van der Waals radius; for the de mapping (Fig. S4.2b), the ESP surface near F2* atom can be seen as uniformly distributed area with light red color which shows the distance of F2* to surface is shorter than its van der Waals radius. [Note: In order to show the surface better, only one F atom (F2*) from the other molecule is shown.]

Hirshfeld surface analysis of complex (1) mapped with $\mathrm{d}_{\mathrm{i}}$ (Fig. S4.2a) and $\mathrm{d}_{\mathrm{e}}$ (Fig. S4.2b) represents the proximity of the atom from the mapped surface, from inside of the surface and outside of the surface, respectively. The distance of the atom to the surface is less than van der Waals radius of specific atom, and then the color of the surface is shown in red color. Here the $d_{i}$ plot shows the three red spots, which correspond to the C6, O1 and F4 atoms (clockwise from the bottom), are indicated with arrows (their respective distance to the surface is smaller than van der Waals radius). For the de plot shown in Fig. S4.2b, the ESP surface near F2* atom can be seen as uniformly distributed area with light red color which shows the distance of F2* to surface of the other molecule is shorter than its van der Waals radius. Additionally, the $d_{i}$ and $d_{e}$ Hirshfeld surface maps of complex (2) is similar to those of complex (1).

## 9. Deformation density analysis and Laplacian map


(a)

(b)

Figure S5. (a) Deformation density ${ }^{6}$ analysis ((+ve and -ve values indicated by red and blue colors); and (b) Laplacian map ${ }^{7}$ of the interaction region of $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdBr}_{2}\right](2)$, +ve and -ve values represented by black and pink (where vscc is.) colors. [Note: Deformation density iso-surfaces are drawn at 0.001 au ; the vscc region, which is shown as pink rings, just closely surrounds the central O atom (in red color) in (b).]

## 10. Electrostatic Potential Analysis



Figure S6. Electrostatic potential (ESP) contours $^{8}$ for (a) t-[(3-4FH-py) $\left.)_{2} \mathrm{PdCl}_{2}\right](\mathbf{1})$; and (b) t-[(3-4FHpy) ${ }_{2} \mathrm{PdBr}_{2}$ ] (2), showing the presence of electron negative region (red concentric circles area) between the fluorine and oxygen. [Note: C, O, N, F, Cl, Br and Pd are in grey, red, blue, yellow, green, brown and dark green color, respectively. The method of B3LYP/LANL2DZ level of theory is used for all the ESP related calculations.

## 11. Crystal data

Table S3. Crystal data of both compounds

|  | $\mathrm{t}-\left[(3-4 \mathrm{FH}-\mathrm{py})_{2} \mathrm{PdCl}_{2}\right](\mathbf{1})$ | t-[(3-4FH-py) $\left.\mathrm{PdBr}^{2}\right](\mathbf{2})$ |
| :---: | :---: | :---: |
| CCDC No. | 1948936 | 1948937 |
| Chemical formula <br> $M_{r}$ <br> Crystal system, space group Temperature (K) | $\begin{aligned} & \mathrm{C}_{18} \mathrm{H}_{18} \mathrm{Cl}_{2} \mathrm{FsN}_{2} \mathrm{O}_{2} \mathrm{Pd} \\ & 623.64 \\ & \text { Monoclinic, } P 2_{l / n} \\ & 100.0(2) \end{aligned}$ | C18H18Br2F8N2O2Pd <br> 712.56 <br> Monoclinic, $P 2_{1 / n}$ <br> 100.0(2) |
| $a, b, c(\AA)$ | $\begin{aligned} & 7.0691 \text { (2), } 18.6278 \text { (5), } \\ & 8.7985 \text { (3) } \end{aligned}$ | $7.2992 \text { (3), } 18.6059 \text { (7), } 8.7965$ <br> (4) |
| $\beta$ | 109.625 (1) | 110.215 (2) |
| $V\left(\AA^{3}\right)$ | 1091.30 (6) | 1121.05 (8) |
| Z | 2 | 2 |
| Radiation type | Mo $K \alpha$ | Mo $K \alpha$ |
| $\mu\left(\mathrm{mm}^{-1}\right)$ | 1.18 | 4.48 |
| Crystal size (mm) | $0.44 \times 0.40 \times 0.06$ | $0.24 \times 0.22 \times 0.16$ |
| Data collection |  |  |
| Diffractometer | Bruker APEX-II CCD | Bruker APEX-II CCD |
| Absorption correction | Multi-scan <br> Bruker SADABS, 1996 | Multi-scan <br> Bruker SADABS, 1996 |
| $T_{\text {min }}, T_{\text {max }}$ | 0.844, 0.971 | 0.713, 0.971 |
| No. of measured, independent, and observed $[I>2 \sigma(I)]$ reflections | 11039, 2398, 2195 | 27252, 2473, 2394 |
| $R_{\text {int }}$ | 0.040 | 0.041 |
| $(\sin \theta / \lambda)_{\text {max }},\left(\AA^{-1}\right)$ | 0.641 | 0.641 |
| Refinement |  |  |
| $R\left[F^{2}>2 \sigma\left(F^{2}\right)\right], w R\left(F^{2}\right), S$ | 0.021, 0.050, 1.05 | 0.015, 0.037, 1.06 |
| No. of reflections | 2398 | 2473 |
| No. of parameters | 152 | 153 |
| $\Delta \rho_{\text {max }}, \Delta \rho_{\text {min }}\left(\mathrm{e} \AA^{-3}\right)$ | 0.45, -0.60 | 0.46, -0.64 |

Computer programs: Bruker Instrument Service v2012.12.0.3, SAINT V8.35A (Bruker AXS Inc., 2015), XT, VERSION 2014/4, SHELXL2013 (Sheldrick, 2013), shelXle (C.B. Huebschle, rev 740), WinGX publication routines (Farrugia, 1999).

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