Electronic Supplementary Information

The Intramolecular Blue-shifting C-H···F-C Hydrogen Bond: Crystal Structure of [4,4′-bis($HCF_2CF_2CF_2CF_2CH_2OCH_2$)-2,2′-bpy]$MCl_2$ Where M = Pt, Pd†

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Supplementary information **A-D** is listed below. Supplementary information **A** and **B** contains the Newman projections and structural descriptions of complex **3**, respectively. Supplementary information **C** lists the calculation results of the geometrical parameters and C-H stretching bands of complex **3**. Supplementary information **D** shows the π-π spacing of complex **3**.

Supplementary info **A**

For compound **3**, its structure and the Newman projections along C13-C14, C14-C15, C19-C20, and C20-C21 are shown in Fig. S1.

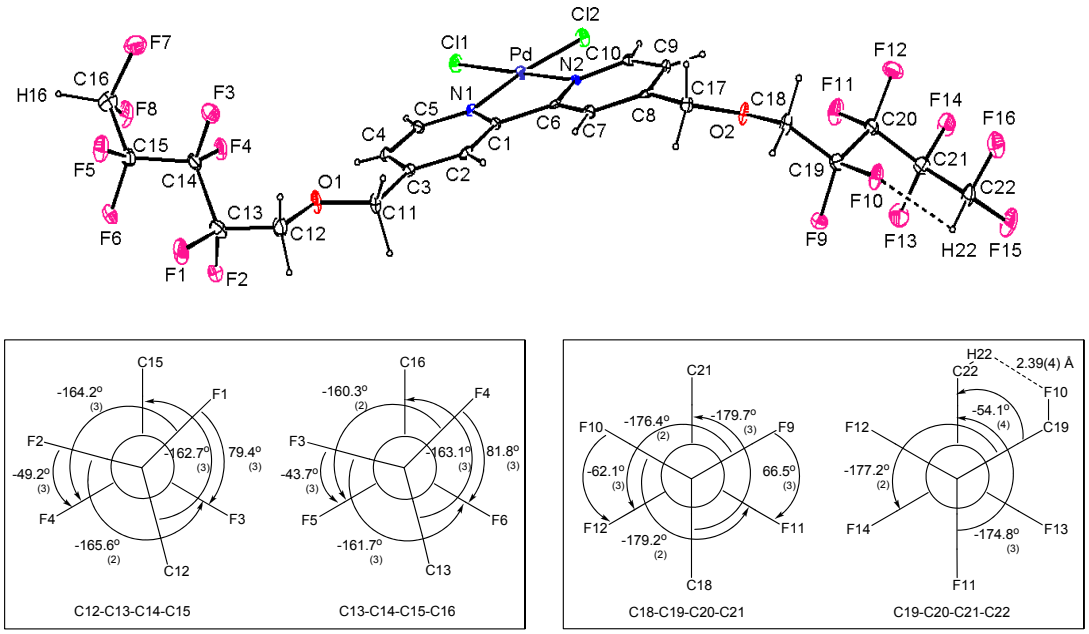

Fig. S1 Molecular plot of **3**. Selected bond lengths [Å] and angles [°]: H22…F10 2.39(4); C22-H22…F10 110(2); C22...F10 2.836(4); C19-F10 1.371(3); C19-F9 1.351(3) C22-H22 0.91(4); C16-H16 1.13(4). Insets: Newman projections of **3**.

Supplementary info **B**

Reported earlier by us, the structure of **3** (CCDC 613935) was refined one more time in this manuscript, with new data set re-collected at 100 K to final R = 0.031. Different from the earlier results that include only calculated hydrogen positions for all H atoms, the current results have the positional parameters of two terminal H atoms at HCF_2-group refined and their temperature factors riding according to the respective neighboring C atoms. The atom labels, with the exception of Pd, were the same as those used in **2**. In our early studies, compound **3** was found to be a very useful recyclable catalyst for use in Pd catalyzed C-C bond forming reactions, along with other fluorous analogs. The structure of **3** was included then just to establish the fact that the distal fluorous ponytails were extending away from the catalytic Pd center. As **3** is isostructural to **2**, it also exhibits the six-membered, intramolecular C-H…F-C hydrogen-bond system in one of the $HCF_2CF_2CF_2CF_2CH_2$ main chains. The C18-C19-C20-C21 fragment has a *transoidal* conformation, torsion angle being -179.7(3)°; and the adjacent C19-C20-C21-C22 a *cisoidal* conformation, torsion angle being -54.1(4)°. The terminal H22 on C22 is very close to F10 on C19, the distance being 2.39(4) Å. The remaining $HCF_2CF_2CF_2CF_2CH_2$- main chain maintains the Gladysz type *transoidal* form.

Supplementary info **C**

The geometrical parameters and the C-H stretching bands of complex **3**.

Table S1. Geometrical parameters of **3** relevant to the C-H···F-C interaction

Distance	Exp. (in Å, X-ray)	Calc. (in Å)
H22···F10	2.39(4)	2.438
C22-H22	0.91(4)	1.105
C16-H16	1.13(4)	1.108
C19-F10	1.371(3)	1.400
C19-F9	1.351(3)	1.384

Table S2. The C-H stretching bands (in cm^{-1}) of **3** and the assignments

Exp.	Calc.		Assignment
	unfactored	factored*	
3123	3074	3120	Pyridyl C-H's
	3067	3113	
3092	3042	3087	
3076	3034	3080	
	3013	3058	
	3013	3058	
3002	2956	3000	HCF_2, H bonded
2950	2912	2956	HCF_2, free
2932	2896	2939	Methylene C-H's
	2887	2930	
2894	2847	2890	
	2840	2883	
	2838	2881	
	2832	2874	
2855	2807	2849	
2825	2799	2831	

*The scaling factor is 1.015.

Supplementary info **D**
The side view of the fluorous ponytailed bpy planes in the crystal structure of **3**.

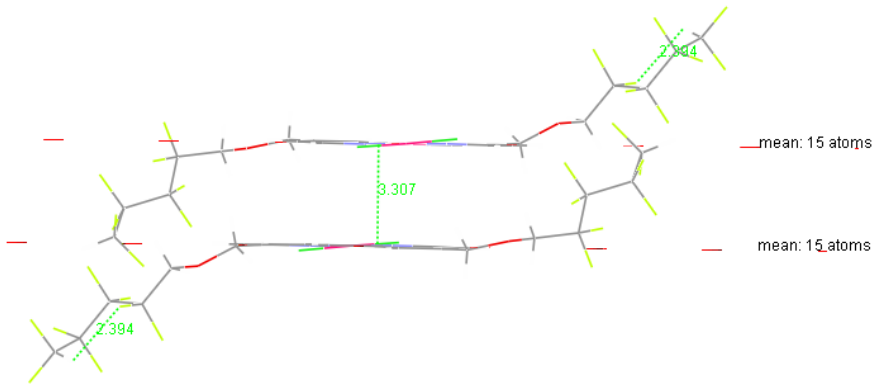

Fig. S2. The interactions along the normal of bpy planes in the crystal structure of **3**. The separation between bpy planes is 3.307(4) Å. A bpy plane was defined by the C and N atoms of bpy and $PdCl_2$.