Electronic Supplementary Information

Temperature and pressure variations of d-d luminescence band maxima of bis(pyridylalkenolato)palladium(II) complexes with different ligand substituents: opposite-signed trends

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Table of contents

Table S1 Calculated optimized structure of [Pd{PyCHC(CH_3)O}$_2$] in the gas-phase, singlet ground state.

Atoms	X	Y	Z
Pd	0.00000900	-0.00003100	0.00020900
O	0.35579100	2.00404200	0.00029900
O	-0.35582000	-2.00408700	0.00009300
N	2.03488100	-0.45377400	0.00007300
N	-2.03485300	0.45379500	0.00029400
C	1.56138600	2.58691800	-0.00030700
C	-1.56143900	-2.58692400	-0.00024300
C	2.38069900	-1.78465400	0.00063600
C	3.03926000	0.51386100	-0.00049700
C	-2.38066900	1.78468800	0.00075700
C	-3.03925700	-0.51382100	-0.00032100
C	2.78656600	1.93008700	-0.00092700
C	1.48565300	4.10468800	-0.00011600
C	-2.78658300	-1.93005000	-0.00040300
C	-1.48573000	-4.10468600	-0.00027400
H	1.53293900	-2.47331900	0.00104900
C	3.70523500	-2.23498800	0.00060400
C	4.41025800	0.08062700	-0.00059100
H	-1.53289900	2.47332600	0.00122800
C	-3.70520500	2.23502200	0.00054800
C	-4.41024300	-0.08057400	-0.00074000
H	3.67943500	2.56182200	-0.00151900
H	0.93507300	4.45622800	0.89181300
H	0.93294500	4.45646000	-0.89058600
H	2.48909800	4.55956500	-0.00123000
H	-3.67946400	-2.56176700	-0.00063900
H	-0.93301500	-4.45621600	-0.89087100
H	-0.93516400	-4.45648200	0.89152500
H	-2.48917900	-4.55955400	-0.00152600
H	3.90827800	-3.30904100	0.00102600
C	4.74951200	-1.27288000	-0.00005600
H	5.18611700	0.85251600	-0.00100200
H	-3.90823100	3.30907800	0.00100800
C	-4.74948500	1.27292300	-0.00031200
H	-5.18610400	-0.85246000	-0.00138500
H	5.79979900	-1.58323200	-0.00011300
H	-5.79976800	1.58329200	-0.00065800

Table S2 Calculated optimized structure of [Pd{PyCHC(CH_3)O}$_2$] in acetone, singlet ground state.

Atoms	X	Y	Z
Pd	-0.00000300	-0.00000200	-0.00018800
O	0.35767700	2.00373200	-0.10305600
O	-0.35764500	-2.00373700	0.10263600
N	2.03626400	-0.45626800	-0.00964700
N	-2.03627000	0.45627400	0.00942100
C	1.56456700	2.59020100	-0.02285900
C	-1.56455700	-2.59020500	0.02268600
C	2.38534900	-1.78774700	-0.05611800
C	3.04030700	0.51185800	0.02915000
C	-2.38533300	1.78777300	0.05553000
C	-3.04032800	-0.51186200	-0.02861200
C	2.78607000	1.93014600	0.04795900
C	1.48982500	4.10711600	-0.02154400
C	-2.78609200	-1.93014900	-0.04753800
C	-1.48979500	-4.10711700	0.02110600
H	1.54188500	-2.48083500	-0.08227500
C	3.71087700	-2.23542300	-0.05392000
C	4.41208400	0.08129200	0.04395100
H	-1.54185200	2.48086700	0.08105400
C	-3.71086200	2.23544500	0.05387400
C	-4.41211800	-0.08131100	-0.04264800
H	3.67812500	2.56035200	0.10340100
H	0.89064600	4.45875300	0.83854600
H	0.98883100	4.46581100	-0.93928000
H	2.49243900	4.55921200	0.03575800
H	-3.67816800	-2.56035400	-0.10267000
H	-0.88986400	-4.45854600	-0.83853200
H	-0.98960100	-4.46602600	0.93920600
H	-2.49235700	-4.55921000	-0.03713900
H	3.91692300	-3.30792100	-0.09247800
C	4.75365300	-1.27215800	0.00314000
H	5.18748800	0.85223100	0.08225000
H	-3.91688800	3.30796100	0.09204000
C	-4.75366900	1.27215100	-0.00211200
H	-5.18754200	-0.85226800	-0.08017800
H	5.80362400	-1.58111800	0.01220500
H	-5.80364900	1.58110000	-0.01057800

Table S3 Calculated optimized structure of [Pd{PyCHC(C_3F_7)O}$_2$] in the gas-phase, singlet ground state.

Atoms	X	Y	Z
Pd	0.00000000	0.00000000	0.00000000
F	3.35113300	-1.87800100	2.57586500
F	3.85233000	-3.59019700	1.14050000
F	4.52837500	-0.07855100	0.48542100
F	5.27911300	-2.00591700	-0.48840400
O	1.67999000	-0.77579600	0.82617800
N	-0.04107800	-1.44178100	-1.51019800
C	-1.03970200	-1.33380800	-2.44847600
H	-1.71281700	-0.48508900	-2.31711500
C	-1.19806500	-2.24297100	-3.50256900
H	-2.01502600	-2.09698400	-4.21344000
C	-0.29304100	-3.32665100	-3.61266400
H	-0.38791400	-4.05920700	-4.42030200
C	0.73006300	-3.44049000	-2.66637000
H	1.45269900	-4.26022300	-2.71764000
C	0.86952900	-2.49106700	-1.60425300
C	1.97049700	-2.67681300	-0.68720200
H	2.60615800	-3.54509800	-0.87485200
C	2.29731400	-1.87005000	0.38223000
C	3.55211200	-2.19675200	1.19768500
C	4.84823100	-1.43502300	0.73560000
C	6.07027600	-1.44111900	1.72248300
F	6.35046700	-2.73291500	2.18442400
F	7.21237100	-0.95750700	1.06661200
F	5.83288300	-0.61556900	2.82819800
F	-3.35113300	1.87800100	-2.57586500
F	-3.85233000	3.59019700	-1.14050000
F	-4.52837500	0.07855100	-0.48542100
F	-5.27911300	2.00591700	0.48840400
O	-1.67999000	0.77579600	-0.82617800
N	0.04107800	1.44178100	1.51019800
C	1.03970200	1.33380800	2.44847600
H	1.71281700	0.48508900	2.31711500
C	1.19806500	2.24297100	3.50256900
H	2.01502600	2.09698400	4.21344000
C	0.29304100	3.32665100	3.61266400
H	0.38791400	4.05920700	4.42030200
C	-0.73006300	3.44049000	2.66637000
H	-1.45269900	4.26022300	2.71764000

C	-0.86952900	2.49106700	1.60425300
C	-1.97049700	2.67681300	0.68720200
H	-2.60615800	3.54509800	0.87485200
C	-2.29731400	1.87005000	-0.38223000
C	-3.55211200	2.19675200	-1.19768500
C	-4.84823100	1.43502300	-0.73560000
C	-6.07027600	1.44111900	-1.72248300
F	-6.35046700	2.73291500	-2.18442400
F	-7.21237100	0.95750700	-1.06661200
F	-5.83288300	0.61556900	-2.82819800

Table S4 Calculated optimized structure of [Pd{PyCHC(C_3F_7)O}$_2$] in acetone, singlet ground state.

Atoms	X	Y	Z
Pd	0.00000000	0.00000000	0.00000000
F	3.33124300	-1.99047800	2.56472200
F	3.89668700	-3.60257000	1.04259600
F	4.47049300	-0.04343800	0.56505000
F	5.29832600	-1.90076100	-0.47463200
O	1.65717900	-0.81687400	0.84530400
N	-0.07173900	-1.45544100	-1.50211100
C	-1.09895700	-1.36682100	-2.41210200
H	-1.78239600	-0.52953100	-2.26527600
C	-1.26914000	-2.27673300	-3.46450200
H	-2.10769700	-2.14648200	-4.15253900
C	-0.34540400	-3.34070700	-3.60574300
H	-0.44615200	-4.07021600	-4.41446300
C	0.70376700	-3.43920300	-2.68506300
H	1.43781100	-4.24636800	-2.75916500
C	0.84906800	-2.49296600	-1.62205300
C	1.96831100	-2.67514300	-0.72307500
H	2.61454500	-3.52835000	-0.94146900
C	2.28747500	-1.89289800	0.36531600
C	3.54644500	-2.22383400	1.16709100
C	4.82512900	-1.40016400	0.76423200
C	6.02732700	-1.41119300	1.77667800
F	6.31948100	-2.70994300	2.21374500
F	7.17619000	-0.89347500	1.16003300
F	5.75190200	-0.61912500	2.89781500
F	-3.33124300	1.99047800	-2.56472200
F	-3.89668700	3.60257000	-1.04259600
F	-4.47049300	0.04343800	-0.56505000

F	-5.29832600	1.90076100	0.47463200
O	-1.65717900	0.81687400	-0.84530400
N	0.07173900	1.45544100	1.50211100
C	1.09895700	1.36682100	2.41210200
H	1.78239600	0.52953100	2.26527600
C	1.26914000	2.27673300	3.46450200
H	2.10769700	2.14648200	4.15253900
C	0.34540400	3.34070700	3.60574300
H	0.44615200	4.07021600	4.41446300
C	-0.70376700	3.43920300	2.68506300
H	-1.43781100	4.24636800	2.75916500
C	-0.84906800	2.49296600	1.62205300
C	-1.96831100	2.67514300	0.72307500
H	-2.61454500	3.52835000	0.94146900
C	-2.28747500	1.89289800	-0.36531600
C	-3.54644500	2.22383400	-1.16709100
C	-4.82512900	1.40016400	-0.76423200
C	-6.02732700	1.41119300	-1.77667800
F	-6.31948100	2.70994300	-2.21374500
F	-7.17619000	0.89347500	-1.16003300
F	-5.75190200	0.61912500	-2.89781500

Table S5 DFT calculated Pd-L distances for the two [Pd{PyCHC(R)O}$_2$] compounds (R = CH_3 and R = C_3F_7).

R =	Pd-L	Distances (Å)		
		XRD	PBEPBE/Lanl2dz	PBEPBE/Lanl2dz (PCM)
CH_3	Pd-N	2.055	2.085	2.087
	Pd-O	1.984	2.035	2.038
C_3F_7	Pd-N	2.027	2.088	2.093
	Pd-O	1.981	2.027	2.032

Table S6 Experimental and calculated Raman shifts for [Pd{PyCHC(C_3F_7)O}$_2$].

Experimental Raman shift (cm^{-1}) at 293 K	**Variation (cm^{-1}/K)**	**Calculated Raman shift (cm^{-1})**	**Assignation**
200	-0.017	203	γPd-N + γPd-O + γC-H (enol)
262	-0.027	254	γPd-N + γC-H (pyridine) + γC-H (enol)
288*	-0.007	295	γC-H (enol) + γC-H (pyridine)
305	-0.005	333	C-F scissor mode
319	+0.014	349	δC-C(-N)-C + δC-F
377	-0.003	485	νPd-O + δC-F + γC-H (pyridine)
545	-0.006	532	νPd-O + νC-F + δC-F
588	-0.012	579	γC-H (enol) + γC-H (pyridine) + δC-F
633	+0.019	652	νPd-O + νC-F + γenol + νPd-N
654	-0.007	657	γenol + νC-C (C_3F_7) + νC-F
749	+0.002	776	γC-H (pyridine) + γC-H (enol)
815	-0.005	826	γC-H (enol) + γC-H (pyridine)
879	-0.016	855	τC-C (pyridine) + τC-C (enol) + γC-H(enol) + γC-H (pyridine)
1024	-0.016	999	νC-F + γC-H (pyridine) + τC-C (pyridine)
1271	-0.019	1303	δC-H (pyridine) + νC-N
1313	-0.004	1342	νC=N + δC-H (enol) + δC-H (pyridine)
1485	-0.005	1440	δC-H (enol) + δC-H (pyridine) + νC=O
1542	0	1545	νC-C (pyridine) + δC-H (pyridine) + δC-C (pyridine) + νC-N + νC-C (enol)
1604	+0.006	1603	νC-C (pyridine) + δC-H + δC-C
1621	-0.016	1629	νC=C (enol)
3080	-0.024	3188, 3178, 3169, 3164, 3148	νC-H (pyridine or enol)
3107	-0.014	3188, 3178, 3169, 3164, 3148	νC-H (pyridine or enol)

*at 200 K, ν indicates stretch; δ, in-plane bend; γ, out-of-plane bend and τ, torsion

Table S7 Experimental and calculated Raman shifts for [Pd{PyCHC(CH_3)O}$_2$].

Experimental Raman shift (cm^{-1}) at 293 K	Variation (cm^{-1}/K)	Variation (cm^{-1}/kbar)	Calculated Raman shift (cm^{-1})	Assignation
211	-0.006		244	νPd-O + δC-C (CH_3)
274	-0.015		264	γC-H (enol) + γC-C (enol) + γC-H (pyridine) + γC-C (pyridine) + γPd-N
413	+0.004		384	νPd-O + νC-C (CH_3) + δC-H (enol) + δC-H (pyridine)
611	+0.004		648	τC-C (pyridine) + νPd-N + δC-H (pyridine)
656	+0.004		672	τC-C (pyridine) + νPd-O + νC-C(CH_3)
778	-0.004		804	γC-H (enol) + γC-H (pyridine)
867	-0.004		853	νC-N + τC-C (pyridine) + δC-H (pyridine) + δC-H (enol) + δC-H(CH_3)
956	-0.004		943	νC-C(CH_3) + νC-O
1017	-0.007	+0.431	1055	δC-H (pyridine)
1283	-0.018		1305	δC-H (pyridine) + δC-H (enol) + νC-N
1401	-0.002		1428	C-H scissor mode (CH_3) + δC-H (enol) + δC-H (pyridine) + νC-O
1513	-0.014	+0.376	1535	νC=C (pyridine) + νC-N (pyridine) + δC-H (pyridine) + νC=C (enol) + δC-H (enol) + C-H scissor mode (CH_3)
1586	-0.013	+0.325	1602	νC=C (enol) + νC=C (pyridine) + δC-H (pyridine) + δC-H (enol) + δC-C (pyridine)
1609	-0.008		1612	νC=C (enol) + νC=C (pyridine) + δC-H (pyridine) + δC-H (enol) + δC-C (pyridine)
2911	0	+0.595	2986	νC-H (CH_3)
3076	0	+0.844	3138	νC-H (pyridine) or νC-H (enol)

ν indicates stretch; δ, in-plane bend; γ, out-of-plane bend and τ, torsion

Table S8 Intermolecular distances closest to the palladium center and R groups in the crystal structure. Distances calculated from published structures at room temperature.[1]

CH_3		C_3F_7	
Intermolecular distance of closest atoms from palladium			
Bond	***Distance (Å)***	***Bond***	***Distance (Å)***
Pd-C3	*5.21*	Pd-C3	*4.34*
Pd-H3	*5.57*	Pd-H3	*4.59*
Pd-C4	*4.19*	Pd-C4	*3.54*
Pd-H4	*3.85*	Pd-H4	*3.37*
Pd-C5	*4.09*	Pd-C5	*3.76*
Pd-C6	*3.59*	Pd-C6	*3.76*
Pd-H6	*3.12*	Pd-H6	*3.25*
Pd-C7	*4.26*	Pd-C7	*4.75*
Pd-C8	*4.50*	Pd-C8	*5.36*
Pd-H8	*3.83*	Pd-F8	*4.70*
Intermolecular distance of closest atoms from R groups (CH_3 and C_3F_7)			
C1-H8 (of CH_3)	*2.80*	C1-F8 (of CF_2)	*3.37*
C2-H8 (of CH_3)	*3.15*	C2-F8 (of CF_2)	*3.52*
C3-H8 (of CH_3)	*3.57*	C3-F8 (of CF_2)	*3.57*
C1-C8 (of CH_3)	*3.67*	C1-C8 (of CF_2)	*4.00*
C2-C8 (of CH_3)	*3.89*	C2-C8 (of CF_2)	*3.89*
C3-C8 (of CH_3)	*4.06*	C3-C8 (of CF_2)	*4.13*
C4-C8 (of CH_3)	*4.04*	C4-C8 (of CF_2)	*4.50*
C5-C8 (of CH_3)	*3.88*	C5-C8 (of CF_2)	*4.63*
N-C8 (of CH_3)	*3.67*	N-C8 (of CF_2)	*4.37*

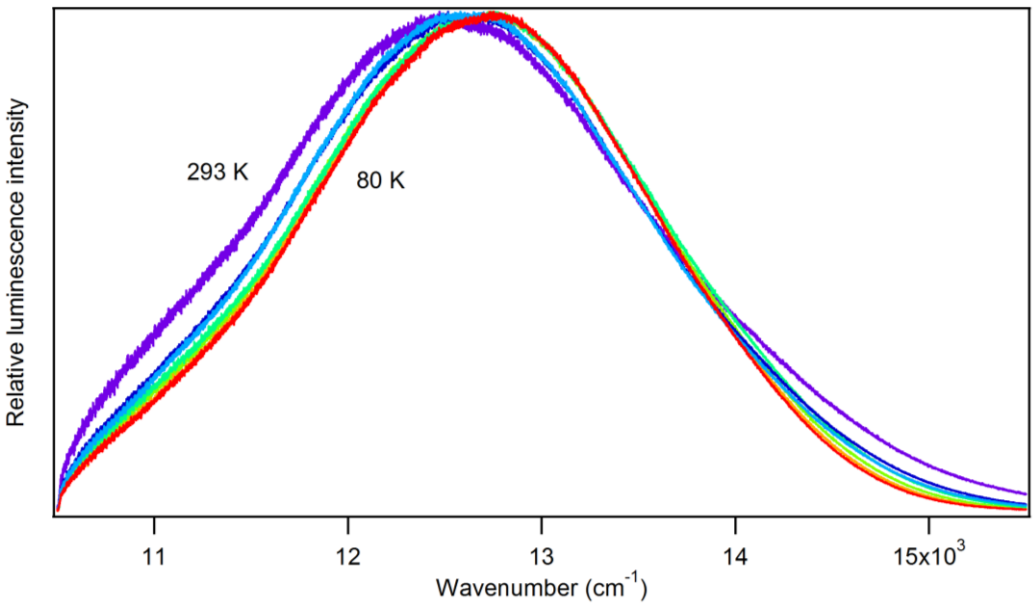

Fig. S1 Temperature-dependent luminescence spectra of [Pd{PyCHC(C_3F_7)O}$_2$] shown at 80, 100, 125, 175, 180, 200 and 293 K (red to blue). Band maxima are set to identical height to illustrate the shift with temperature.

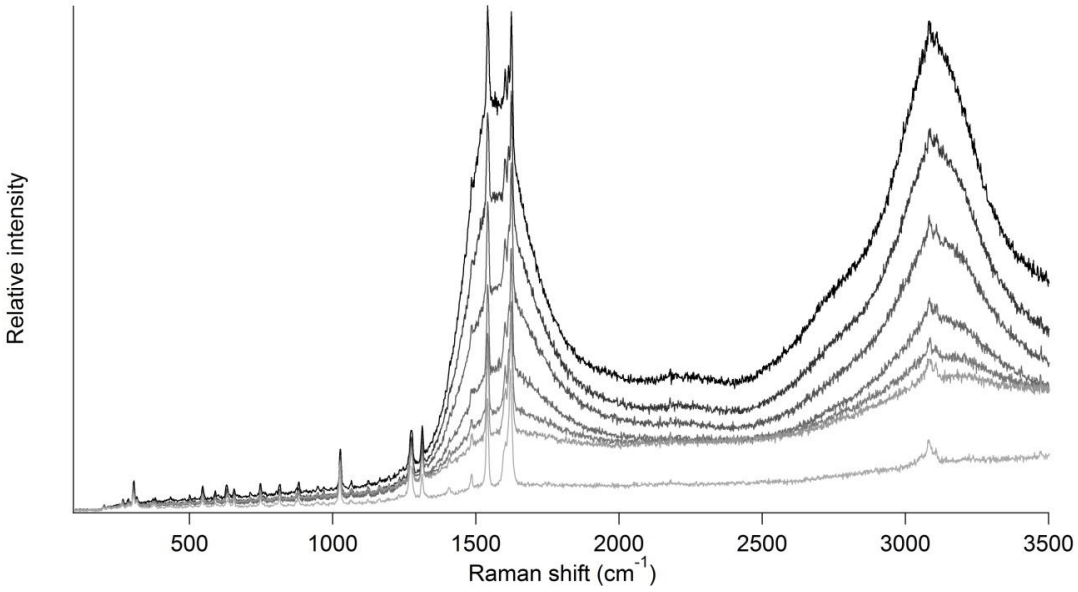

Fig. S2 Temperature-dependent Raman spectra of [Pd{PyCHC(C_3F_7)O}$_2$] shown at 80, 100, 125, 150, 175, 200 and 293 K (dark to light).

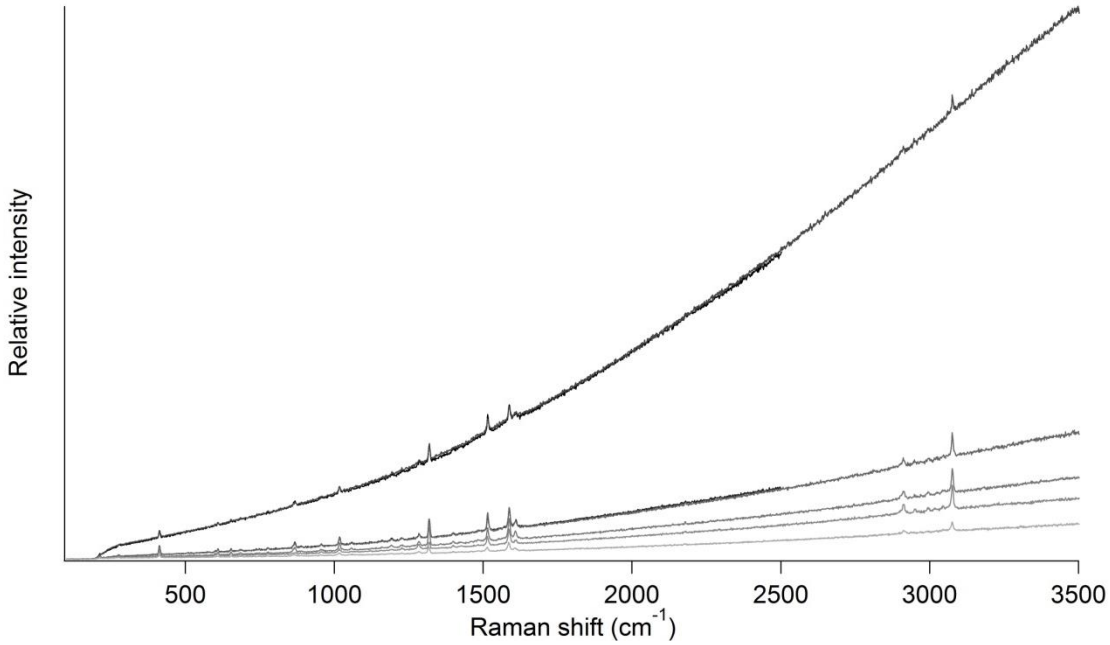

Fig. S3 Temperature-dependent Raman spectra of [Pd{PyCHC(CH_3)O}$_2$] shown at 80, 100, 125, 150, 175, 200 and 293 K (dark to light).

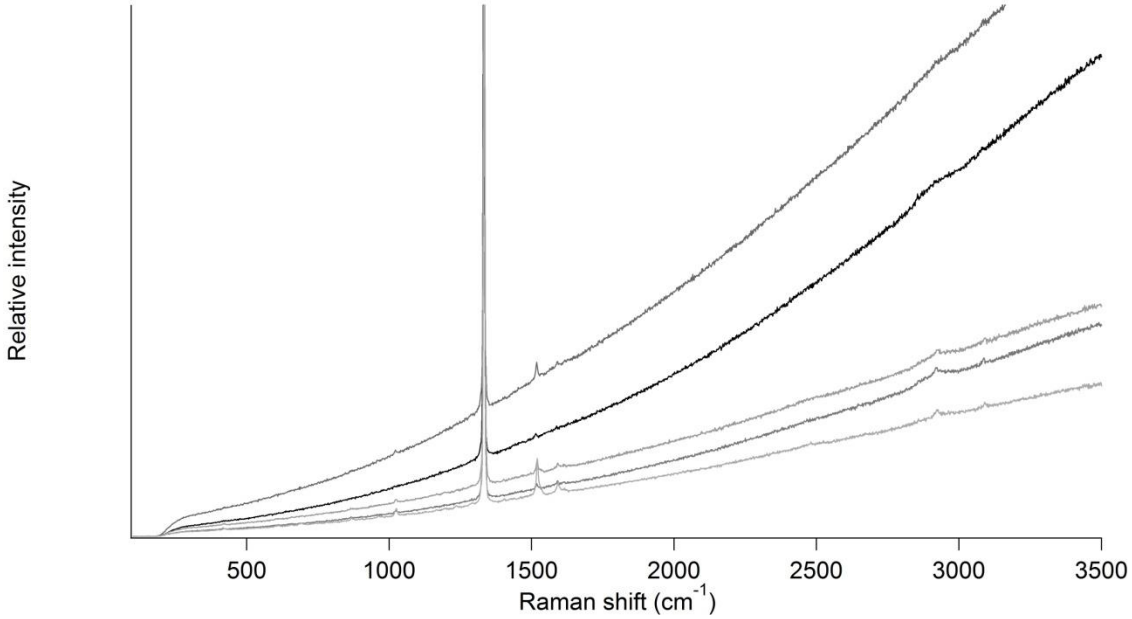

Fig. S4 Pressure-dependent Raman spectra of [Pd{PyCHC(CH_3)O}$_2$] shown at 6, 13, 15, 19 and 20 kbar (dark to light).

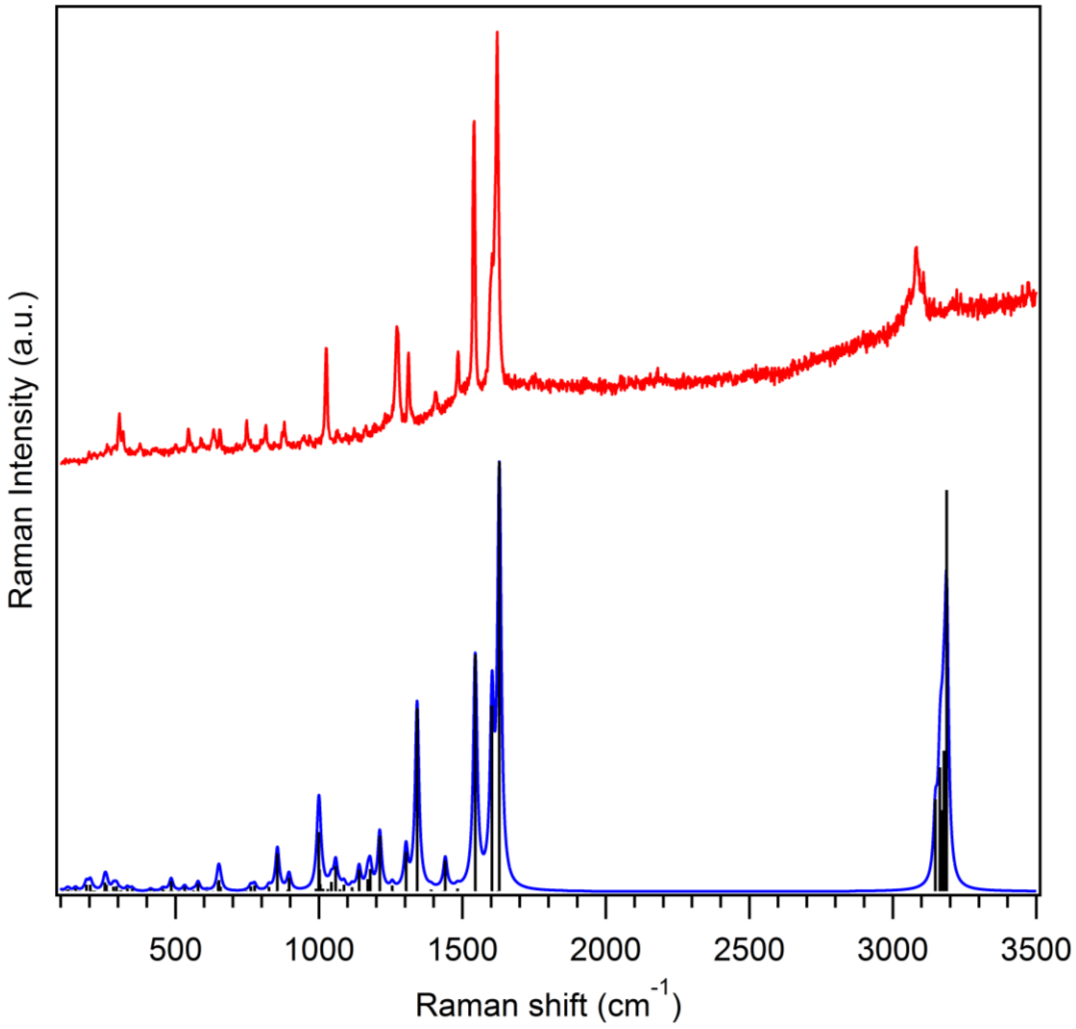

Fig. S5 Comparison between the experimental Raman spectrum of [Pd{PyCHC(C_3F_7)O}$_2$] (red) and the theoretical Raman spectrum calculated with DFT in the gas-phase (blue, PBEPBE/Lanl2dz). The vertical black lines represent the calculated transitions. Their full-width-at-half-maximum was set to 8 cm^{-1} to yield the blue spectrum. The spectra were normalized and offset along the y-axis for clarity.

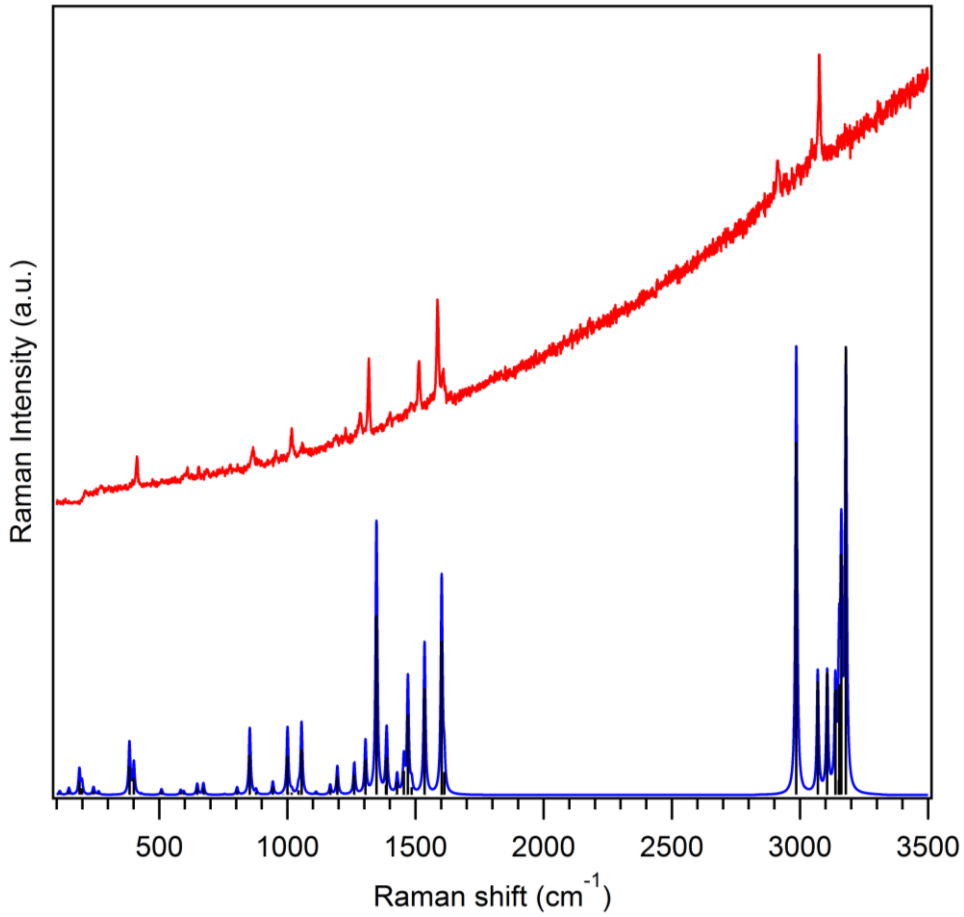

Fig. S6 Comparison between the experimental Raman spectrum of [Pd{PyCHC(CH_3)O}$_2$] (red) and the theoretical Raman spectrum calculated with DFT in the gas-phase (blue, PBEPBE/Lanl2dz). The vertical black lines represent the calculated transitions. Their full-width-at-half-maximum was set at 4 cm^{-1} to yield the blue spectrum. The spectra were normalized and offset along the y-axis for clarity.

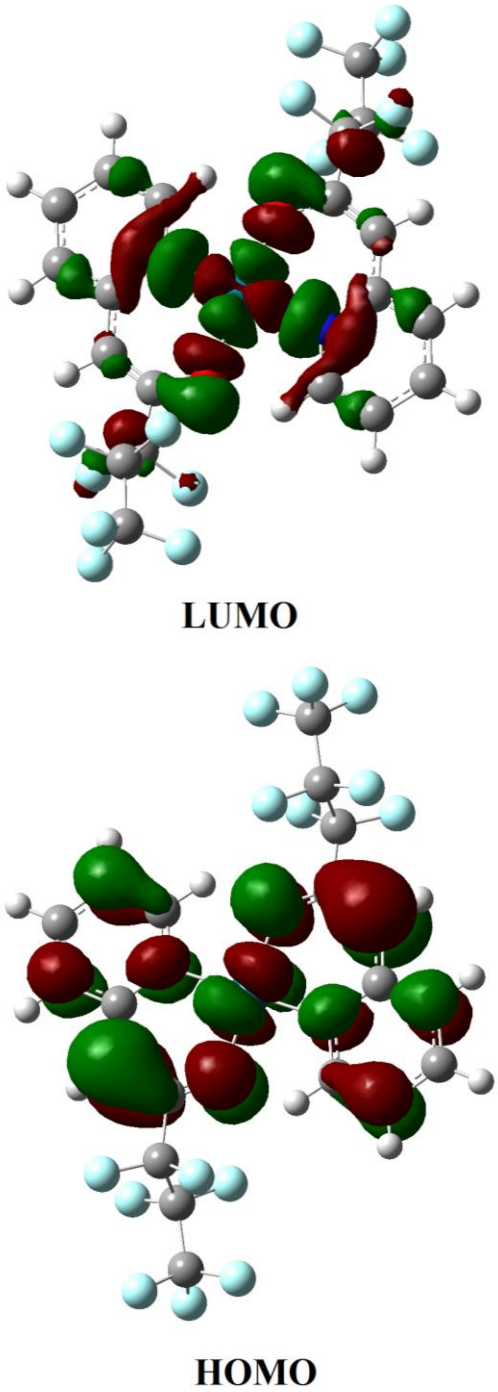

Fig. S7 LUMO (top) and HOMO (bottom) for [Pd{PyCHC(C_3F_7)O}$_2$] visualized with an isovalue of 0.02 atomic units.

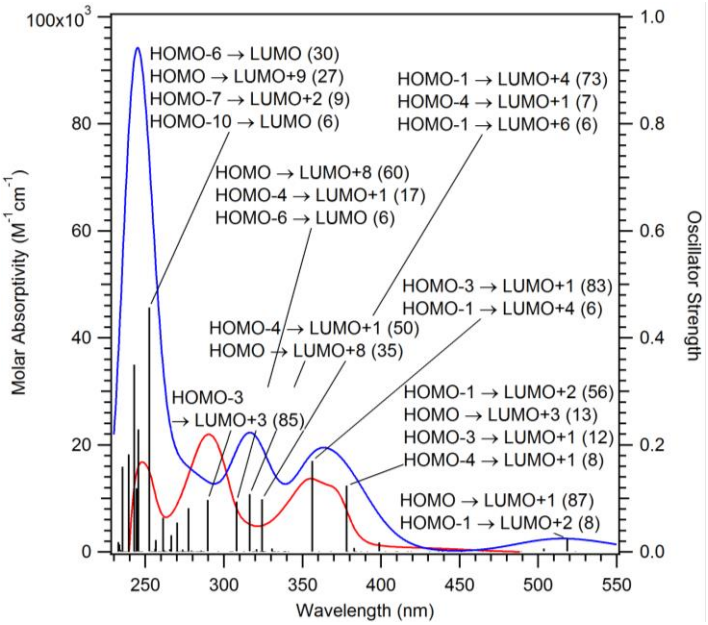

Fig. S8 Comparison between the experimental absorption spectrum in acetone of [Pd{PyCHC(C_3F_7)O}$_2$] (red) and the theoretical absorption spectrum calculated by TD-DFT in acetone by mean of the polarizable continuum model (PCM) (blue, PBEPBE/Lanl2dz). The vertical black lines represent the calculated transitions with their oscillator strength given on the right axis. Their full-width-at-half-maximum was set at 1300 cm^{-1} to yield the blue spectrum.

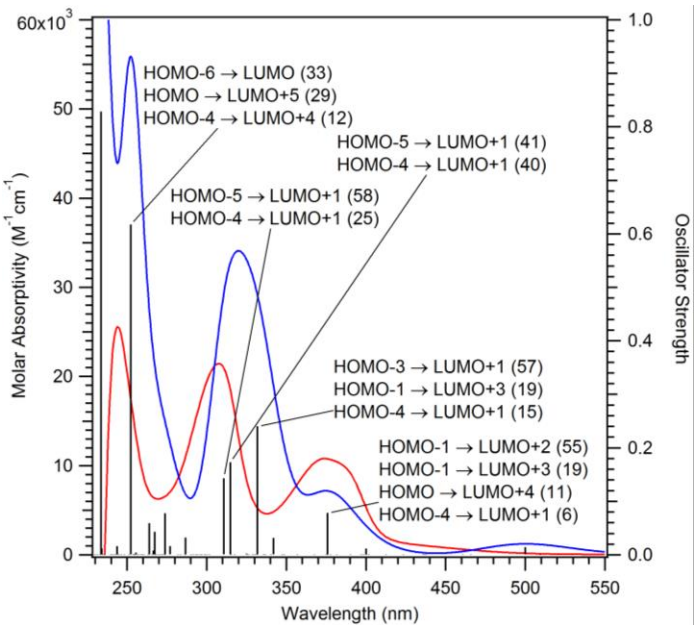

Fig. S9 Comparison between the experimental absorption spectrum in acetone of [Pd{PyCHC(CH_3)O}$_2$] (red) and the theoretical absorption spectrum calculated by TD-DFT in acetone by mean of the polarizable continuum model (PCM) (blue, PBEPBE/Lanl2dz). The vertical black lines represent the calculated transitions with their oscillator strength given on the right axis. Their full-width-at-half-maximum was set at 1300 cm^{-1} to yield the blue spectrum.

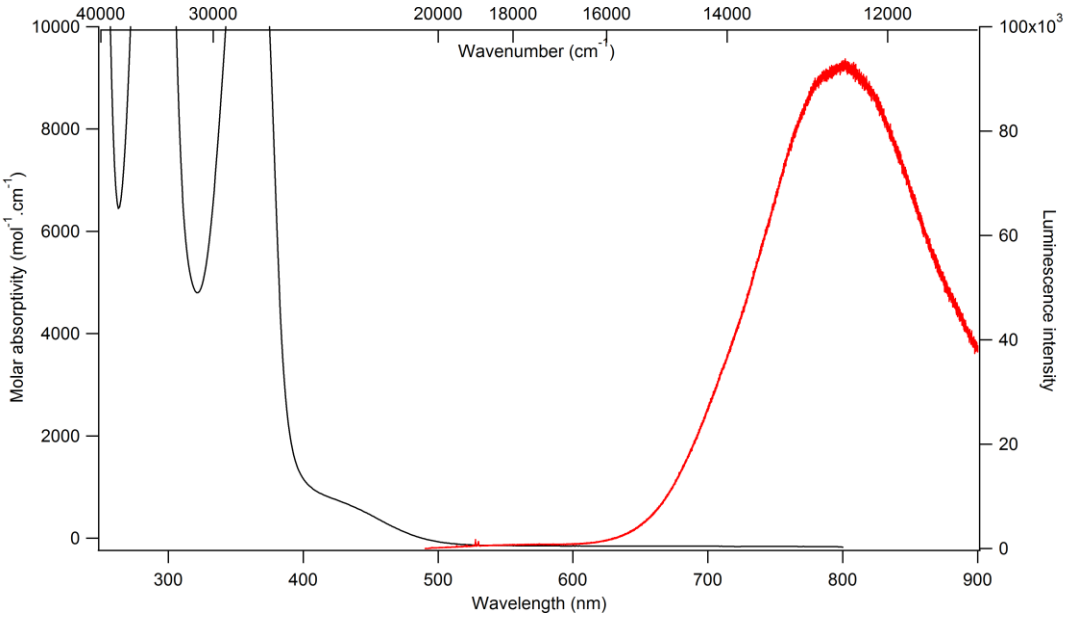

Fig. S10 Superposition of absorption (black solid line) and luminescence spectra (red solid line) of [Pd{PyCHC(C_3F_7)O}$_2$].

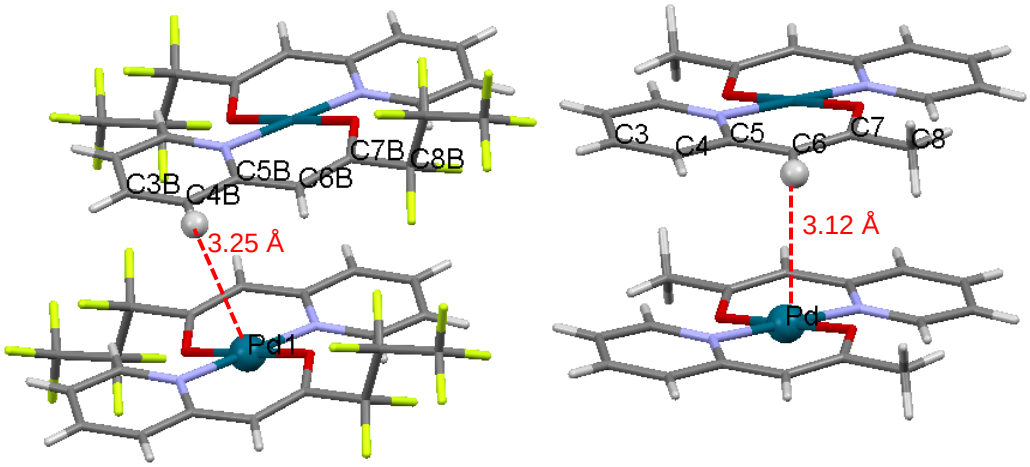

Fig. S11 Systematic views of intermolecular packing of [Pd{PyCHC(C_3F_7)O}$_2$] complex (left) and [Pd{PyCHC(CH_3)O}$_2$] (right). Shortest intermolecular distance is represented on top figure for both compounds. Atom labels are from published cif files (room temperature).

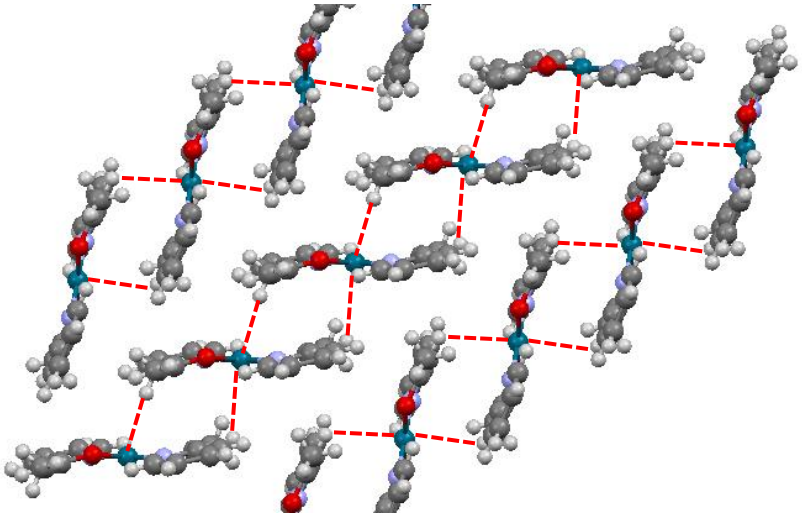

Fig. S12 View of intermolecular packing including Pd···H-C interaction (red) in [Pd{PyCHC(CH_3)O}$_2$] complex.

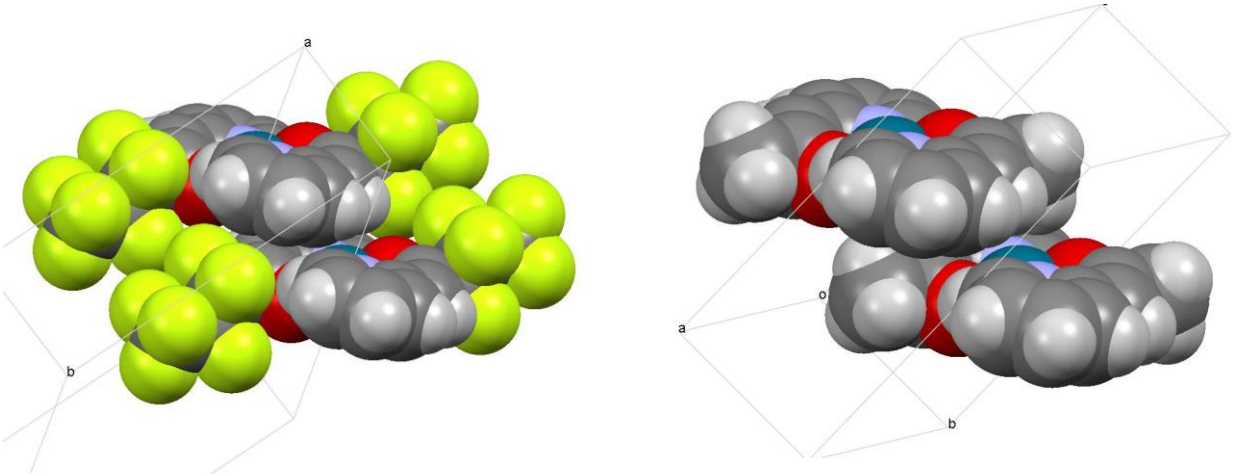

Fig. S13 Spacefill views of intermolecular packing of [Pd{PyCHC(C_3F_7)O}$_2$] complex (left) and [Pd{PyCHC(CH_3)O}$_2$] (right).

Experimental details (X-ray powder diffraction)

Experimental powder X-ray diffraction patterns were recorded at 20ºC in reflection mode on a Bruker D8 Discover diffractometer with the GADDS High-Throughput Screening (HTS) setting, using graphite monochromatized Cu Kα radiation generated at 40 kV and 40 mA. The 2D HI-Star detector was positioned at a distance of 15 cm from the powder sample, which was placed on a glass plate. This allowed simultaneous collection of data over an angular domain up to 35° in 2θ. Measurements were carried out in coupled scan mode (θ-θ geometry). Three separate frames were collected with a scanning time of 30 min/frame and intensity along each measured diffraction arc was integrated to create the 1D powder pattern of intensity versus 2θ, over the angular range 4° < 2θ < 70°. The structural data from single-crystal analyses[1] retrieved in CIF format were used to calculate theoretical powder X-ray diffraction patterns with the aid of the Mercury software[2].

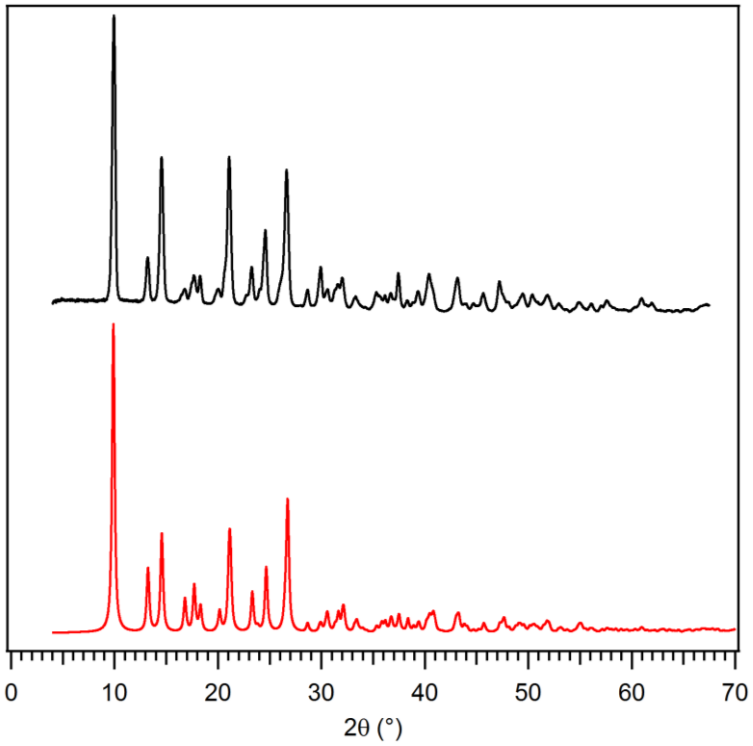

Fig. S14 Experimental (black) and calculated[1] (red) powder XRD patterns for [Pd{PyCHC(CH_3)O}$_2$].

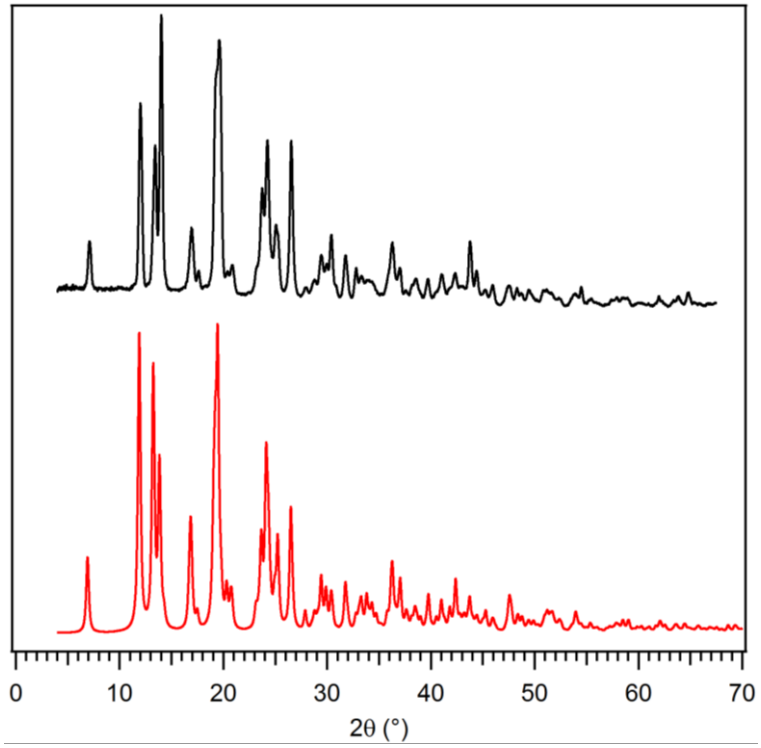

Fig. S15 Experimental (black) and calculated[1] (red) powder XRD patterns for [Pd{PyCHC(C_3F_7)O}$_2$].

Reference

[1] L. Brückmann, W. Tyrra, S. Stucky and S. Mathur, *Inorg. Chem.* **2012**, *51*, 536-542.

[2] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.* **2006**, *39*, 453-457.