Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supporting Information (ESI) for the manuscript:

Structurally characterized dipalladium(II)-oxamate metallocyclophanes as efficient catalysts for sustainable Heck and Suzuki reactions in ionic liquids

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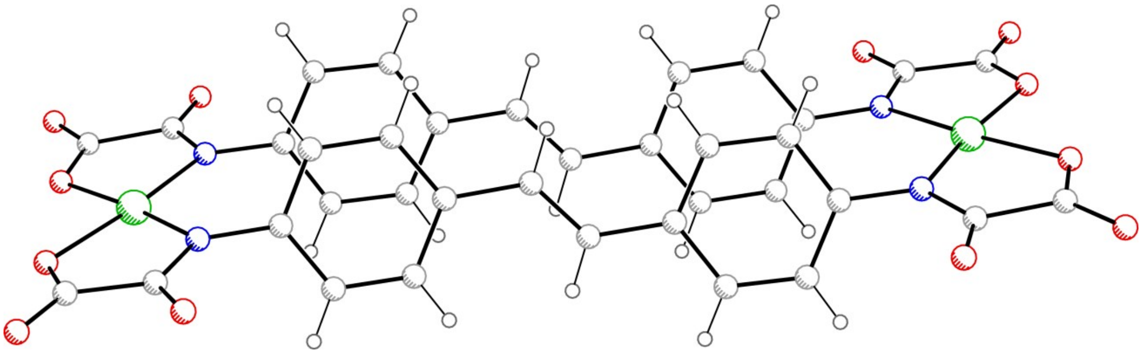
Structural details

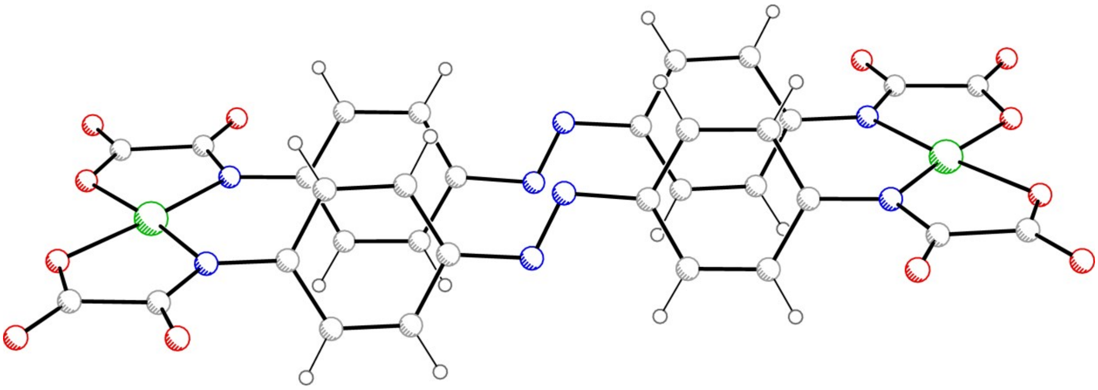
(n-NBu$_4$)$_4$[Pd$_2$(dpvba)$_2$] · 6MeOH · 2Et$_2$O (2a), (n-NBu$_4$)$_4$[Pd$_2$(dpazba)$_2$] · 8MeOH (3a) and (n-NBu$_4$)$_2$[Pd$_2$(dpeba)$_2$] ·8MeOH (4a)

The basal plane defined by the N$_2$O$_2$ donor sets at the palladium(II) ion and the respective mean planes of the oxamate fragments [O(1)-O(2)-O(3)-N(1)-C(1)-C(2) and O(4a)-O(5a)-O(5a)-N(2a)-C(17a)-C(18a)] are practically coplanar in **2a** and **3a** [dihedral angles of 3.8(3) and 3.0(3)º (**2a**) and 4.0(4) and 1.4(4)° (**3a**)], whereas they form angles of 7.1(1) and 4.5(1)° in **4a**. The two phenyl rings of the diphenylvinyl (**2a**) and azobenzene (**3a**) groups are almost coplanar [dihedral angles of 1.6(2) (**2a**) and 4.9(4)º (**3a**)] while in **4a** they are not [dihedral angle of 7.4(1)°]. These rings form, with the basal plane, angles of 62.2(1)/62.4(1), 61.3(2)/61.8(3) and 62.0(1)/65.2(1)° in **2a**, **3a** and **4a**, respectively

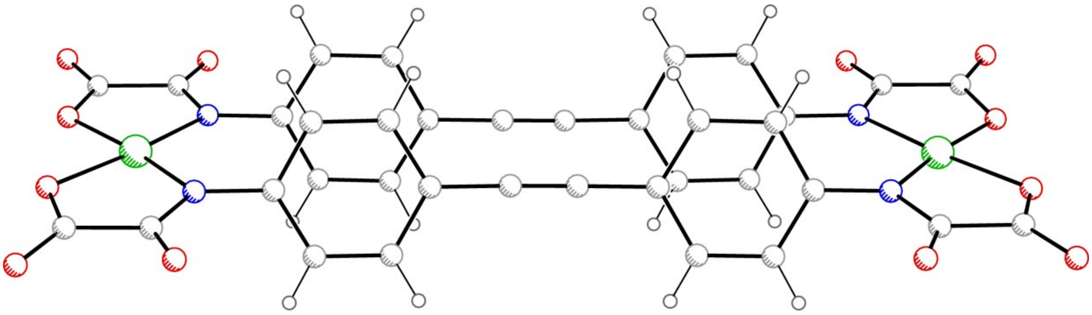
Intramolecular π-π stacking interactions between the aromatic rings of the [Pd$_2$(dpvba)$_2$]$^{4-}$, [Pd$_2$(dpazba)$_2$]$^{4-}$ and [Pd$_2$(dpeba)$_2$]$^{4-}$ entities occur in **2a**, **3a** and **4a**, the values of the centroid to plane distances of two opposite rings being 3.193(2) (**2a**), 3.189(2) (**3a**) and 3.297(1) Å (**4a**) (Figure S1).



2a

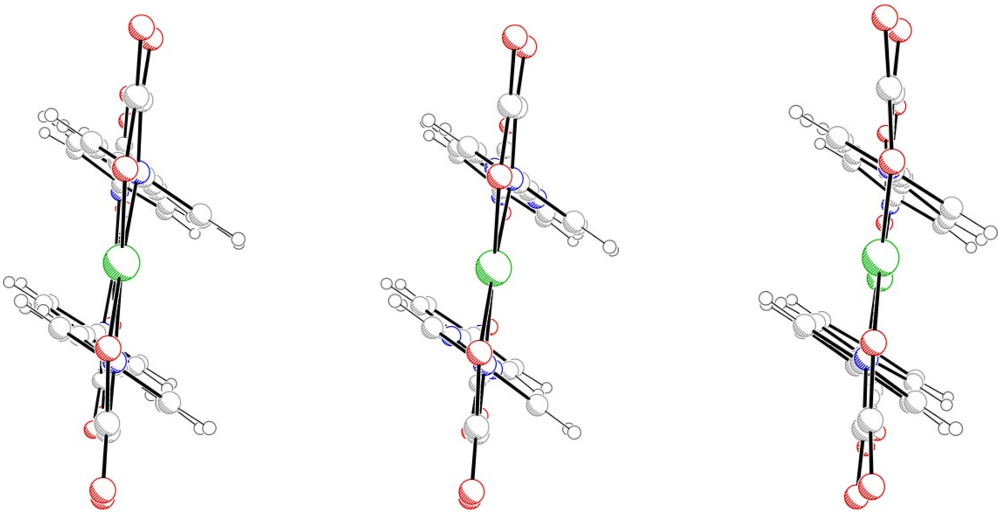


3a



4a

Figure S1. A view along the direction perpendicular to the phenyl planes in order to highlight the π-π interactions for **2a**- **4a**.



2a **3a** **4a**

Figure S2. A view of the dipalladium(II) anionic units along the internuclear Pd-Pd axis for **2a**- **4a.**

The C(9)-C(10) bond length in **4a** is 1.199 (3) Å, a value which is as expected for a carbon-carbon triple bond.

Two methanol molecules are attached by hydrogen bonds to some of the outer oxamate-oxygens [O3m)···O(3) = 2.658(7) (**2a**), 2.659(10) (**3a**), 2.684(3) Å (**4a**) and O(1m)···O(6) = 2.630(8) (**2a**), 2.70(2) (**3a**), 2.668(2) Å (**4a**)]. The remaining methanol molecules (two in **3a** and **4a** and one in **2a**) are linked to these attached molecules [O(2m)···O(1m) = 2.63(1) (**2a**), 2.89(3) (**3a**), 2.750(2) (**4a**) and O(4m)···O(3m) = 2.71(2) (**3a**), 2.819(3) (**4a**) Å] (see Table S2).

The tetra-*n*-butylammonium cations in **2a**-**4a** adopt the usual tetrahedral shape and are located between the layers of the dipalladium(II) complex anions, the bulky organic cations ensuring the isolation of the complex anions from each other in the crystal packing (Figures S3-S5).

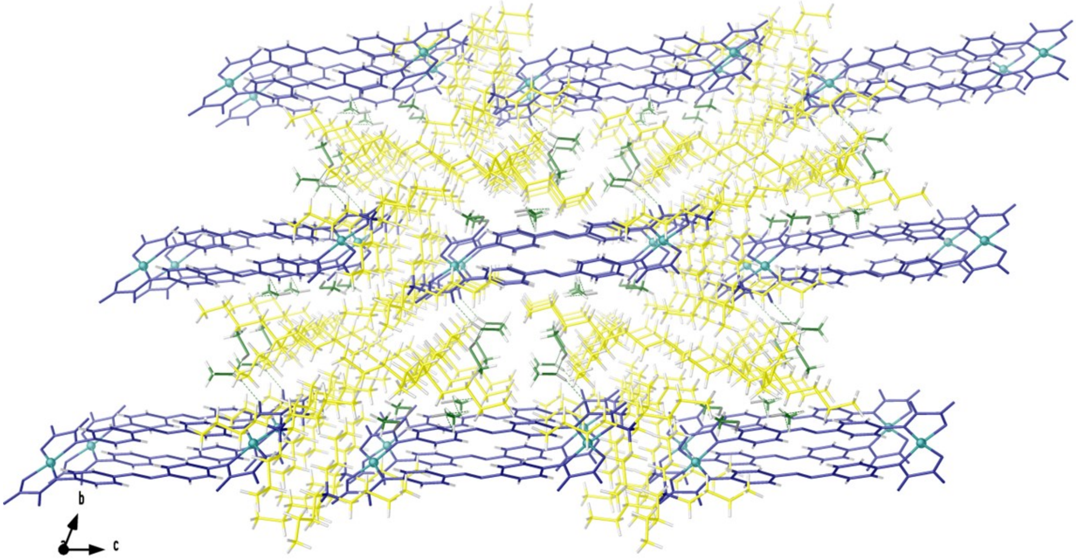


Figure S3. Projection of the crystal packing of **2a** in the crystallographic *bc* plane showing the relative positions of the anionic complexes (blue) and organic cations (yellow). The solvent molecules of crystallization were omitted for clarity.

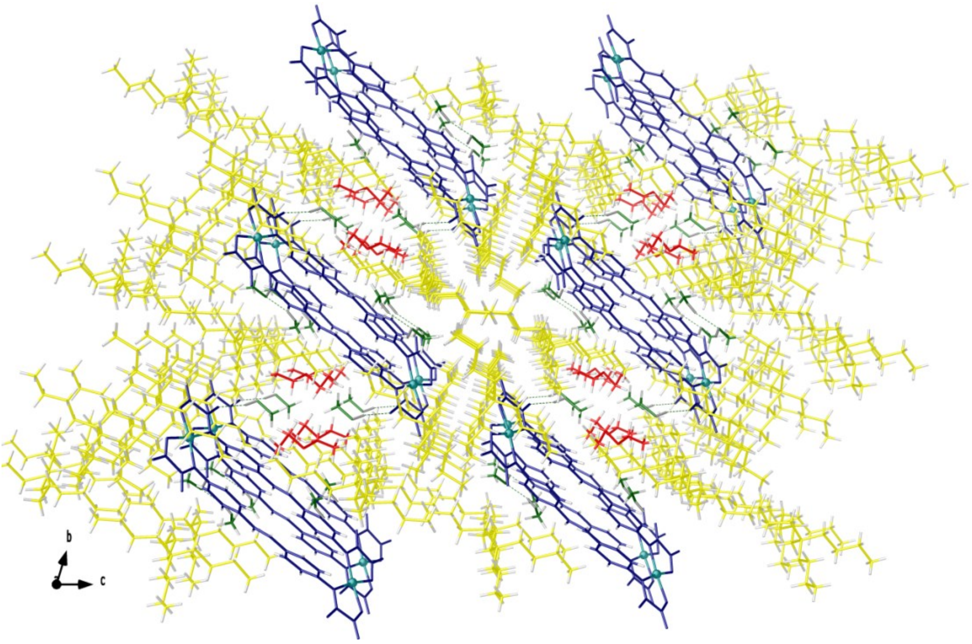


Figure S4. Projection of the crystal packing of **3a** showing the relative positions of the anionic complexes (green) and the organic cations (orange). The solvent momecules were omitted for clarity.

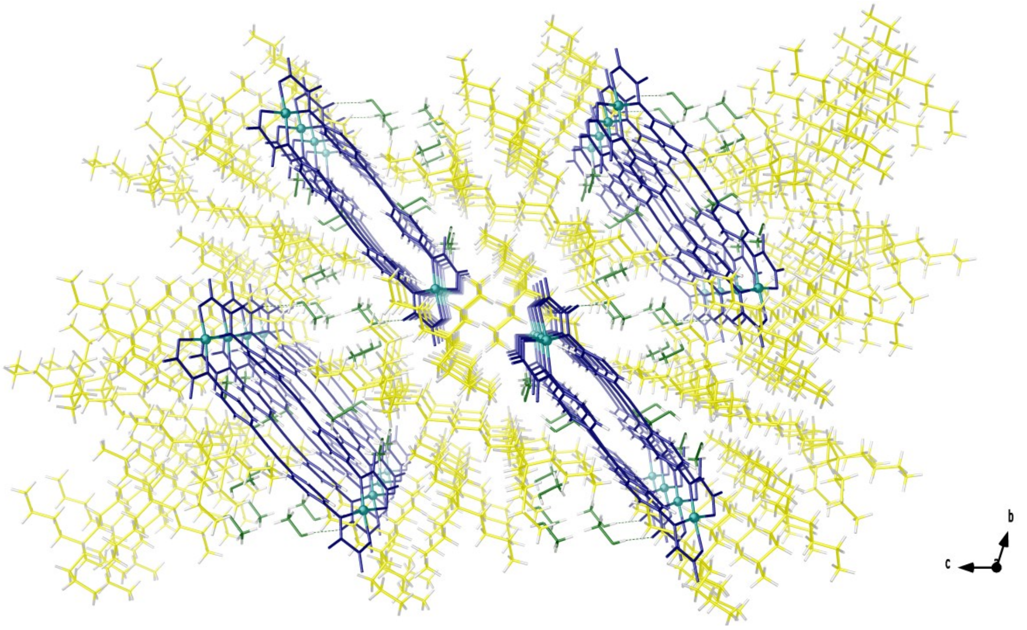


Figure S5. Projection of the crystal packing of **4a** in the crystallographic *bc* plane showing the relative positions of the dipalladium(II) complex anions (green) and the organic tetrabutylammonium cations (orange). The solvent molecules were omitted for clarity.

Table S1. Selected bond distances (Å) and angles (deg) for compounds **2a**-**4a**[&]

	2	**3**	**4**
Pd(1)-N(1)	2.022(5)	2.033(5)	2.022(2)
Pd(1)-N(2a)	2.027(5)	2.028(6)	2.024(2)
Pd(1)-O(1)	2.011(4)	2.009(5)	2.004(1)
Pd(1)-O(4a)	2.014(4)	2.015(5)	2.012(1)
N(1)-Pd(1)-O(1)	81.2(2)	81.3(2)	81.59(6)
N(1)-Pd(1)-O(4a)	171.4(2)	171.8(2)	171.36(6)
N(2a)-Pd(1)-O(1)	171.7(2)	171.5(2)	171.50(6)
N(2a)-Pd(1)-O(4a)	81.7(2)	81.4(2)	81.65(6)
N(2a)-Pd(1)-N(1)	106.9(2)	106.9(2)	106.90(7)
O(1)-Pd(1)-O(4a)	90.2(2)	90.4(2)	89.89(6)

[&]Symmetry transformations used to generate equivalent atoms: (a) = 2-*x*, 1-*y*, -*z* (**2a**); (a) = 2-*x*, 1-*y*, 1-*z* (**3a**); (a) = -*x*, -*y*, -*z* (**4a**)

Table S2. Hydrogen bond lengths (Ǻ) and angles (deg) for compounds **2a**-**4a**.

	H···A/A°	**D···A/A°**	**(DHA)/deg**
2a			
O(1m)-H(1m)···O(6)	2.20	2.630(8)	111.4
O(2m)-H(2m)···O(1m)	1.82	2.632(13)	162.4
O(3m)-H(3m)···O(3)	1.84	2.658(7)	164.4
3a			
O(1m)-H(1m)···O(6)	1.96	2.70(2)	146.1
O(2m)-H(2m)···O(1m)	2.05	2.89(3)	177.8
O(3m)-H(3m)···O(3)	1.83	2.659(10)	168.8
O(4m)-H(4m)···O(3m)	1.87	2.71(2)	171.1
4a			
O(1m)-H(1m)···O(6)	1.84	2.668(2)	168.6
O(2m)-H(2m)···O(1m)	1.92	2.750(2)	170.9
O(3m)-H(3m)···O(3)	1.86	2.684(2)	168.5
O(4m)-H(4m)···O(3m)	2.01	2.819(3)	162.2