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Synthesis, characterization and solid-state photoluminescence studies of six alkoxy phenylene ethynylene dinuclear palladium (II) rods.

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Abstract

A rare family of six discreet binuclear [PdCl(PEt$_3$)$_2$] phenylene ethynylene rods with alkoxy side chains (methoxy, ethoxy and heptoxy) have been developed, and, their solid-state photoluminescence results presented and discussed. The shorter bridging ligands are of the general formula $H–C≡C–C_6H_2(R)_2–C≡C–H$ where R = H, OCH_3, OC_2H_5, OC_7H_{15} whereas the longer ones are based on $H–C≡C–C_6H_4–C≡C–C_6H_2(R)_2–C≡C–C_6H_4–C≡C–H$, where R = OCH_3, OC_2H_5. These ligands display increasing length in both the main dimension (backbone length) as well as the number of carbons in the side chains (R, alkoxide side chain) that stem from the central phenylene moiety. The X-ray crystal structures of two of the prepared complexes are reported: one corresponds to a shorter rod 1,4-bis[*trans*-(PEt$_3$)$_2$ClPd-C≡C]-2,5-diethoxybenzene (**6c**), while the second one is associated to a longer rod, the binuclear complex 1,4-bis[*trans*-$(PEt_3)_2ClPd$-4-(-C≡C-C_6H_4-C≡C)]-2,5-diethoxybenzene (**7c**). All new compounds were characterized by NMR spectroscopy (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) as well as ESI-MS(TOF), EA, FTIR, UV-Vis, cyclic voltammetry and solid-state photoluminescence. Our work shows the influence of the alkoxy side chains on the electronic structure of the family of binuclear Pd rods by lowering its oxidation potential. In addition to this, the increase of the length of the bridge results in a higher oxidation potential. Solid state photoluminescence results indicate that Pd complexes are characterized by a marked decrease in both the emission intensity and in the fluorescence lifetime values as compared to their ligands. This behaviour could be due to some degree of ligand to metal charge transfer.

Introduction

Conjugated one-dimensional rods have been the centre of the attention of several recent studies related to the development of molecular electronic devices such as wires, switches or insulators.[1-7] It is well known that the incorporation of transition metal centers enables even finer tuning of the properties of these rods.[8-11]

Transition metal alkynyl complexes, with their ability to perturb electronic properties through metal alkynyl dπ–pπ interactions[12, 13] are primary candidates for the preparation of metallomolecular devices.[14] The added rigid framework provided by the phenyelene ethynylene ligand, as well as the easy processability improves its potential for molecular device preparation using the building block approach, which allows for fine tuning of magnetic, electronic and photoluminescence properties.[9-11, 14, 15] The introduction of side chains in the aromatic moieties has the major advantage of not only increasing solubility,[16, 17] but also, facilitate the preparation of thin films, improve interface with other co-polymers,[18] contribute to electroluminescence enhancement,[19] inhibit chain to chain interactions, and also give more regular polymerizations products,[20] refine emission color shifting in electroluminescent materials,[21] help improve and tune the formation of thin films for photovoltaic cells[22] as well as increase in delocalization an consequently inter-metal communication in binuclear complexes.[23-26]

Moreover, the decrease on the oxidation potential as a result of methyl (donor) β-substitution in thiophene[27] as well as the decrease in the E_g (energy gap,

$E_{HOMO} - E_{LUMO}$) yielded by methoxy (also donor) substitution in phenylene vinylene oligomers was previously reported.[28]

If Pd-σ-alkynyls are often used for the preparation of homometallic[3, 4, 29-33] or heterometallic[34-36] (with the incorporation of Ru, Fe or Ni metal centers) organometallic polymers, the synthesis of discreet binuclear Pd rods is comparatively much more scarce and not so often found in the literature.[5, 37-39]

Previous studies show that [$PdCl_2(PEt_3)_2$] compounds, form square planar systems with the bridging oligophenylyne ligands.[15] Consequently, an increase of the π delocalization from the ring to the metal center would be expected, which could improve the conducting properties of the rod. This co-planarity between metal center and the π system of the ligand is dictated by the ligand as Onitsuka and colleagues reported for 1,4-diethynylbenzene palladium complexes.[40] This report shows that the metal centers are slightly twisted out of the plane because of steric hindrance caused by the phosphane groups of the metal center. As such, choosing a bridging ligand that, in addition to a solid conjugate backbone, also promotes co-planarity and processability is of great importance. As a matter of fact, the structure and geometry of the target systems greatly influence their properties, resulting in an insulator or a conductor molecule.[41-48]

The luminescence properties of organometallic compounds in solution are well-documented.[9-11, 49-59] The inclusion of transition metal moieties gives access to efficient spin-orbit coupling, which, in turn, enables the population of excited states of triplet character and phosphorescence characteristic of organometallic compounds. As such the coordination of the organic compounds to metal centers can enrich the emission properties by enabling access to new excited-state species.[57] Yam and co-workers[52] reported the carbazole bridged dinuclear Pd and Pt rods which were non-emissive in solution (CH_2Cl_2), whereas it showed luminescence in the solid state (77 K) with a decay time of about 2.9 μs. In the case of the platinum analogues, the luminescence was strongly quenched in CH_2Cl_2 solutions. This was evidenced by the short lifetime observed in the solution (< 0.1 μs) as compared to the one measured in the solid state, which was similar to the palladium counterparts. Moreover, when testing glass samples of this series (77 K, EtOH/MeOH 4:1, v/v), luminescence intensity increased drastically, and the lifetime was augmented to 50 μs.

Previous results from our group and others, showed the importance of solid-state photoluminescence studies in the characterization of new photonic hybrid waveguides,[60-62] prompted us to systematically study the effect of substituents attached to bridging ligands on the electronic communication between the two metal centers and on the solid-state photoluminescence efficiency of a new family of binuclear [PdCl(PEt$_3$)$_2$] phenylene ethynylene rods with alkoxy side chains (methoxy, ethoxy and heptoxy). As such, a family of palladium terminated dinuclear rods (Scheme 1, **6a-d**, **7b-c**), based on 1,4-diethynylbenzene derivatives (Scheme 2, **1a-d**, **4b-c**) was prepared and characterized.

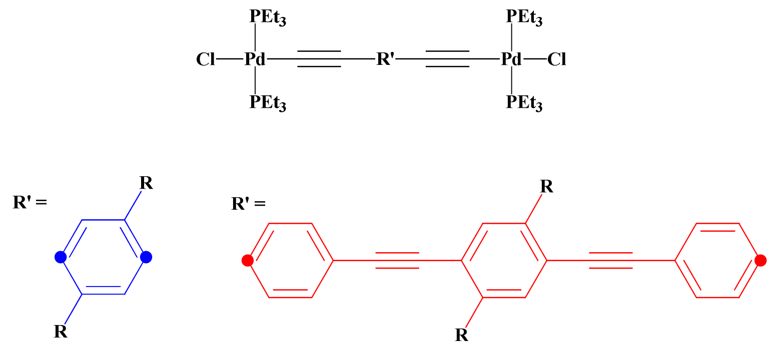
Results and discussion

Synthesis

We have synthesized phenylene ethynylene based bridging ligands of one or three benzene aromatic rings (compounds **1a-d** and **4b-c**, respectively, Scheme 3). In the case of the longer bridging ligands (**4b-c**), the Sonogashira-Hagihara coupling conditions were used (Scheme 3).[19, 41, 48, 62-69] Intermediary products as well as the final products previously reported (**1a-d**)[34, 62, 63] were confirmed at least by ^{1}H and ^{13}C (see Supplementary Information). The yields for these reactions are in the range of those reported in the literature (i.e. 50-76 %).The tris ringed analogues of **1a** and **1d** (R = H and OC$_7$H$_{15}$ respectively **4a** and **4d**), were not prepared by us due to the isolation and purification problems encountered in the synthesis of these ligands. Nevertheless, the numbering was done taking into account these compounds to help the direct comparison among the compounds **1b**/**6b**/**7b** and **1c**/**6c**/**7c**.

The preparation of the palladium rods (**6a-d**, **7b-c,** Scheme 1), was performed with good yields (60 to 80%) by following the methodology reported in the literature[40] and using *trans*-[PdCl$_2$(PEt$_3$)$_2$] (**5**). These rods are sufficiently stable to be washed with water, and two new X-ray structures were obtained for a shorter rod (**6c**) and a longer rod (**7c**) both with the same 1,4-diethoxybenzene central moiety.

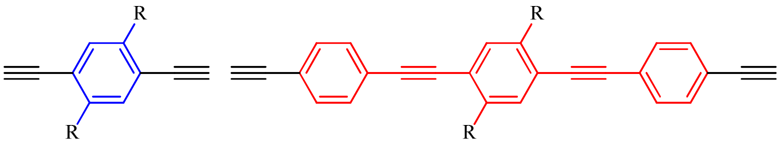
Scheme 1. The series of *trans*-$[PdCl(PEt_3)_2]^+$ rods prepared in this work.



6a: **R** = H
6b: **R** = OCH_3
6c: **R** = OC_2H_5
6d: **R** = OC_7H_{15}

7b: **R** = OCH_3
7c: **R** = OC_2H_5

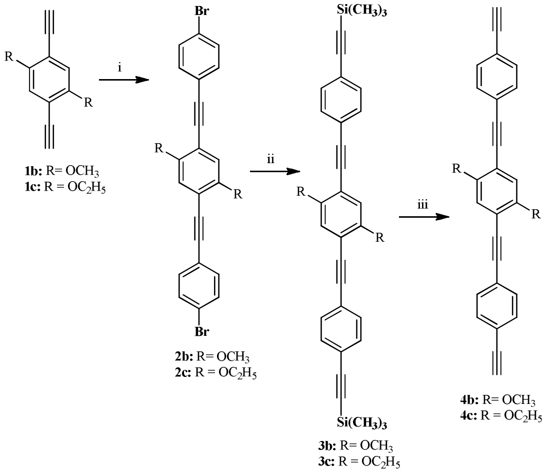
Scheme 2. The 1,4-diethynylbenzene derivatives used as bridging ligands.



1a: R = H
1b: R= OCH_3
1c: R = OC_2H_5
1d: R = OC_7H_{15}

4b: R= OCH_3
4c: R = OC_2H_5

Scheme 3. Preparation of the longer bridging ligands (4b-c); i. Sonogashira-Hagihara coupling, 1-bromo-4-iodobenzene, 45 ºC; ii. Sonogashira-Hagihara coupling, trimethylsilylacetylene, 55ºC; iii. Degassed CH_2Cl_2/CH_3OH (1:1 mixture), KF, room temp.



Characterization

The new compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C{1H} and ^{31}P{^{1}H}) as well as ESI-MS(TOF), EA, FTIR, UV-Vis, cyclic voltammetry and solid-state photoluminescence (see experimental section and Supplementary Information). Briefly, the FTIR studies for the new palladium rods (**6a-d**, **7b-c**) show the characteristic shift on the $\nu_{C\equiv C}$ band with the coordination to the metal. This was also observed by the shift, albeit small, of the singlet observed in the ^{31}P NMR. Furthermore the Pd rods complexes display (in comparison with the free ligands), in the ^{1}H spectrum, mostly shielding of the aromatic (no more than 0.5 ppm) and side chain protons (ca. 0.1 ppm only). The aromatic protons show very similar chemical shifts in comparison with the free ligands (*e.g.* **6b**, OCH_3 6.69 vs. 6.98 ppm in the free ligand). The same observation can be made for the first protons of the side chains (*e.g.* **6b**, OCH_3 3.74 vs. 3.87 ppm in the free ligand). Furthermore, the values for the equivalent protons across Pd rods are relatively closer. This can be observed for the side chains as well as for the aromatic protons. The palladium rods (**6a-d**, **7b-c**) all show ^{31}P NMR singlets at around 18 ppm which is only about 1 ppm more than the free palladium starting material *trans*-[$Pd(PEt_3)_2Cl_2$] (**5**). There is no significant change in this value throughout the series. The main difference in the NMR data of the palladium rods comes from the virtual coupling observed in the ^{13}C NMR. This C–P coupling[70] was found at around 15 ppm in the ^{13}C spectra for all the rods.

The Pd complexes were also characterized by ESI-TOF. A $[M-Cl]^+$ peak was found for most complexes, except for complex **6d**, for which, a peak at 2240.51 *m/z* $[2M+Na+H]^+$ was observed. Furthermore, $[M+Na]^+$ ion peaks were also observed for all the studied compounds. For **6a**, an ion peak of 727.0 *m/z* was found which corresponds to $[M-Cl-PEt_3+H]^+$. Several other ions were visible in the case of the longer complexes. For example, for **7b**, 881.3 *m/z* presents a peak with formal composition $[M-(Pd(PEt_3)_2Cl)+PEt_3]^+$. Similar fragmentation and cleavage is observed in the literature.[35]

UV-vis studies

Significant information about the influence of the chemical structure on the optoelectronic properties of the compounds can be obtained from the analysis of the UV-Vis absorption spectra.[71]

The absorption is dominated by spin allowed $\pi \rightarrow \pi^*$ transitions of the delocalized electronic charge of the ethynelbenzene moeities, which are rich in conjugated bonds. Two main bands are observed for the tris ringed ligands **4b** and **4c** at about 316 and 376 nm. However, the absorption bands of the single ring ligand **1b** are notably blue shifted, showing a maximum at 346 nm (Figure 1). It should be mentioned that the absorption bands of the tris ringed ligands show a red shift when compared with the similar 1,4-diphenylethynylbenzene reported by Nakatsuji,[72] with a peak at 322 nm. Nevertheless, Nakatsuji and co-workers performed this study in $CHCl_3$ solution which might account for the high ε that was observed (62.0×10^3 $M^{-1}cm^{-1}$). No significant change was observed in the position of the absorption bands of **4b** and **4c** compounds. Probably this observation is due to the small difference in length of side chains (OCH_3 to OC_2H_5) of the prepared compounds.

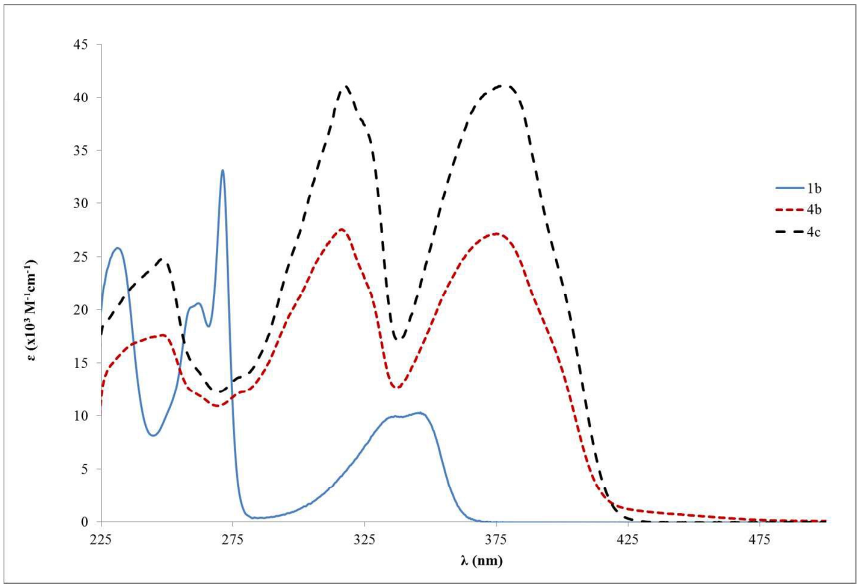


Figure 1. Absorption spectra (ε *vs.* λ) for the shorter (**1b**) and longer free ligands (**4b-c**) in CH_2Cl_2.

Concerning the palladium complexes, the spectra of the palladium rod (**6a**) based on the single ringed free ligand without any side chains (**1a**) is presented and compared to the starting materials in Figure 2. The bands of the absorption spectrum of **6a** can be clearly assigned to those of the starting materials as they show similar positions with a slight blue shift. It seems that the coordination of the bridge to the palladium termini has little effect on the $\pi \rightarrow \pi^*$ absorption bands.

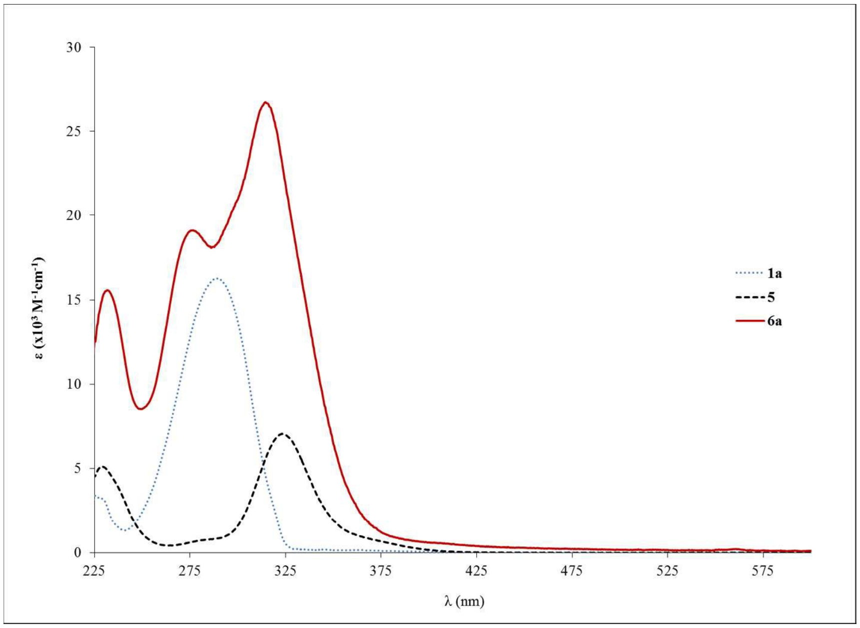


Figure 2. Absorption spectra (ε *vs.* λ) for the palladium rod **6a** as well as the respective free ligand (**1a**) and starting complex **5** in CH_2Cl_2.

In the case of the other palladium rods, the shift is in the expected low energy direction (red shift) as further conjugation is brought about by the coordination. Moreover, the high similarity between the absorption of the starting ligand and the resulting complex is an indication of the predominantly ligand character of the transitions ($\pi \rightarrow \pi^*$) responsible for the absorption spectrum of the complex. This observation was also reported by several other authors[32, 74-79] who additionally admitted some degree of MLCT (metal-to-ligand charge transfer) for the low energy bands ($d_\pi \rightarrow \pi^*(C{\equiv}C{-}R)$) in similar compounds ($ClL_2Pd{-}C{\equiv}C{-}C_6H_4$-R, where R=($C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}PdLCl)_2$ or analogous Pt complexes).

We have analyzed the effect of the length of the ring backbone on the absorption properties. A table, which summarizes the position of the relevant absorption bands for both the ligands and the Pd complexes is available in the Supplementary Information (Table S. 1). In the case of **1b** to **6b** (shorter bridging ligands), the variation is from 346 to 362 nm and for **4b** to **7b** (longer bridging ligands), it changes from 375 to 385 nm which is even lower that the single ringed case. The increase of ε is also lower in the case of the tris ringed rods (**7b-c**, Figure S. 2, about twofold relative to free ligands) when compared to the single ringed counterparts (**6b-d**, about 3 fold in relation to the free ligands). This can point to lesser conjugation which might be due to trapped electron density on the ligand. Furthermore, the increase in side chain length is mostly inconsequential after a length of **6c** (OC_2H_5), in the particular case of the studied alkoxy chains, as only slight variations in the range of 1-5 nm are observed when changing only the alkyl length. Nevertheless, in respect to ε, a marked decrease is observed from **6c** to **6d** (31 to 25 × 10^3 $M^{-1}cm^{-1}$, Figure 3). Finally, the significant differences found both in the positions as well as in the intensities of the absorption bands of the Pd-complexes compared to their associated free ligands are directly related to $\pi \rightarrow \pi^*$ electronic transition properties. It might be an indication of different electronic conduction properties, which are important for optoelectronic applications. Moreover, this point will be further analyzed in the solid-state fluorescence decay studies section.

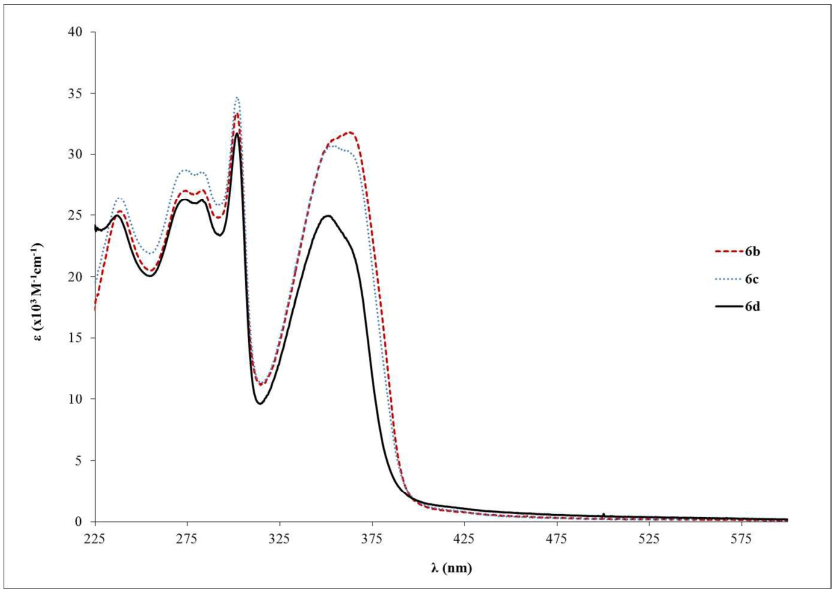


Figure 3. Electronic spectra (ε *vs.* λ) for the palladium rods (**6b-d**) in CH_2Cl_2.

Electrochemistry studies

The free ligands only present an irreversible oxidation wave in the working potential intervals when the side chain is introduced, *i.e.*, the **1a** ligand does not show any oxidation wave, but **1b-d** and **4b-c**, all present high potential oxidations (ca. 1.6V for the shorter – **1a-d**, – and 1.4V for the longer bridging ligands – **4b-c**). This wave is most likely the one-electron oxidation of the phenyl ring which shifts to lower energies by the electron donating effect of the alkoxy side chains. Other authors,[80] working with similar compounds, also have performed the same attribution.

As for the shorter rods (Figure 4, **6a-d**), it is possible to observe the existence of a two electrode processes. The first one corresponds to a reversible process while the second one is probably irreversible. Reduction for the first process is only observable at 100 mVs^{-1} in the compound with the longer side chain (**6d**) but is relatively weak. However, when the scan rate is increased, the reduction is observed more intensely, indicating a following chemical reaction step. The first oxidation wave width of the compounds with alkoxy side chains (**6b-d**) suggest that this conversion is $1e^-$, which can indicate the formation of the Pd^{II}/Pd^{III} pair.[81] A following conversion to Pd^{III}/Pd^{IV} could characterize the process at higher potentials, but once again, the similarity to the free ligands (as observed in the UV studies), as well as the region where it is found, is close to the electrochemical process of the solvent making it difficult to characterize. The first process observed for the rods with smaller side chains (**6a-b**) tends to irreversibility.

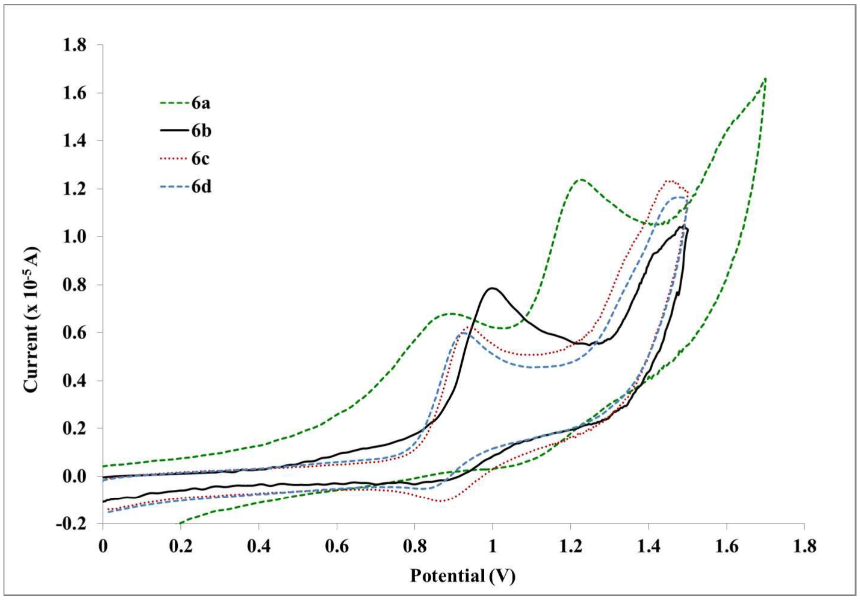


Figure 4. Cyclic voltammograms for the shorter palladium rods without (**6a**) and with alkoxy side chains (**6b-d**) at 100 mVs^{-1} *vs.* Ag/AgCl (KCl saturated) in CH_2Cl_2.

The most striking aspect of the aggregated voltammograms in Figure 4, is that there is a shift to higher anodic potentials when the side chain is introduced (890 (**6a**) to ca. 996 mV for **6b**)**.** This value then shifts back down with the increase of the side chain's length (**6c** and **6d**). This potential appears to stabilize after a side chain of OC_2H_5 (**6c**) since for **6d** (side chain of OC_7H_{15}), the values are very close (945 and 927 mV respectively). Nevertheless, this decrease from OCH_3 to OC_2H_5 side chain is not very pronounced when observing the longer palladium rods, since the anodic potentials for these oxidation processes are already very close (1.31 V for both compounds **7a-b**, Figure 5) and actually higher than that of the **6a** (with no side chain). Moreover, they are very close to the ones observed for the free ligands (**4b-c**). This observation further cements the expected low delocalization not only through the palladium centre but also through these more extended ligands.[82]

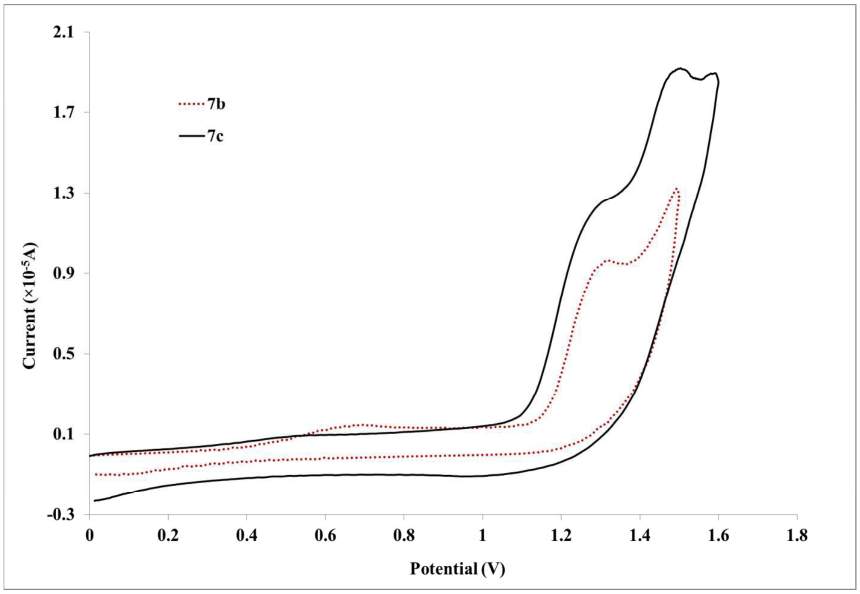


Figure 5. Cyclic voltammograms for the longer palladium rods (**7b-c**) with alkoxy side chains at 100 mVs^{-1} *vs.* Ag/AgCl (KCl saturated) in CH_2Cl_2.

X-ray crystal structure analysis

Two X-ray structures were solved for the prepared Pd rods. One is related with the shorter rod (**6c**) and the other to the analogue longer palladium rod (**7c**). Their ORTEP-3[83] plots are presented in Figure 6 and 7, respectively. A search in the Cambridge Structural Database (CSD)[84] reported only three similar structures.[37, 85] These are related to $PdCl(PR_3)_2$ (where R = butyl, ethyl) rods bridged by 1,4-diethynylbenzene,[37, 85] as well, as another one[37] with the central decorated phenyl ring with OC_8H_{19} side chains similar to the shorter Pd rods reported in this work (**6b-d**). Apart from a published example bearing gold complex termini,[86] no X-ray structure of a dinuclear rod bridged by a tris ringed ligand was found. Table 1 summarizes the crystallographic data for the two reported structures (selected bond angle and distance values are available in the Supplementary Information).

The structure of **6c** (Figure 6) contains half a molecule in the asymmetric unit and, in a first look, there appears to be a co-planarity of the phenylene ring with the palladium center, which has the expected square planar geometry. Nevertheless and although the ring is not twisted in relation to the Pd centre, the coordination plane around the Pd intersects the plane formed by the phenyl ring with an angle of 9.8(3) º. The ethoxy side chain does not run across the same plane formed by the phenylene ring, bending slightly to one side due to, apparently, packing short contacts. In contrast, the free ligand[62] shows co-planar side chains.

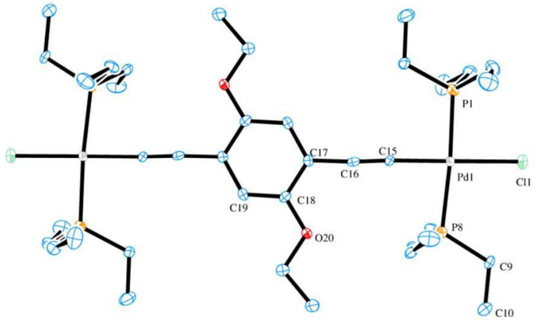


Figure 6. ORTEP-3[83] plot of (**6c**). H atoms are excluded for clarity.

As for bond distances for this structure, C≡C is 1.176(9) Å and Pd–C is 1.964(7) Å which are the typical values for metal-σ-acetylide moieties.[36, 37, 40, 85, 87] Furthermore Pd–P is 2.320(2) Å and Pd–Cl is 2.362(2) Å. Regarding the bridging ligand, C=C and C–O are 1.385(8) - 1.411(9) and 1.385(8) Å long, respectively, which are also similar to other binuclear Pd rods.[37, 85] The Pd–C≡C angle is 175.9(7)º which is in agreement with the expected linear geometry. The P–Pd–Cl angles are 88.17(7) and 96.13(7)º and the P–Pd–C is 177.2(2)º which consequently means a slight deviation from fully square planar geometry. The values for these angles and the corresponding distortion are in good agreement with the previously reported by other authors.[32, 37, 88] Intermolecular interactions commence through short-contacts between the terminal chlorides and the H-atoms from the phosphanes and the ethoxy side chains. The observed packing was very similar to the one observed by Lo Sterzo and co-workers for [Cl(PBu$_3$)$_2$Pd–C≡C]$_2$-1,4-benzene.[37] The same authors reported a sheet like packing when the alkoxy side chain was the longer octyloxy which clearly drives the formation of the lattice.[37] It is noteworthy that this highly oriented lattice comes at a cost of loss of the co-planarity between the Pd centre and the phenylene ring. This could be regarded as a disadvantage for some applications,[89-92] As described by Mayor and co-workers[93], which found, in a family of biphenyl compounds, conductance values thirty times lower when a full torsion (90º) is seen. Further explanation for this observation could also be based in the lack of co-planarity between the central phenyl ring and the two Pd coordination planes.

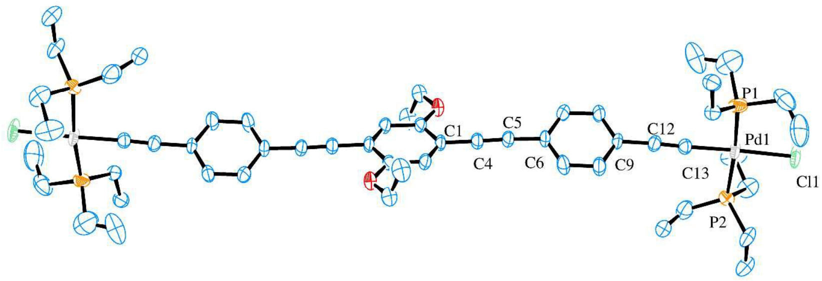


Figure 7. ORTEP-3[83] plot of major component in **7c**. H atoms and disorder are excluded for clarity.

Crystal structure of **7c** shows disorder in all groups coordinated to Pd atom, except the acetylide group (see Supporting Information). The major component (60 % population) is presented in Figure 7. The central and terminal phenyl rings in **7c**, which also contains half a molecule in the asymmetric unit, do not show too much twisting between each other, with the angle formed between the corresponding planes being of only 23.3(2)º. Nevertheless, there is an 86.7(2)º angle (major, 84.2(2)º for the minor component) formed between the central phenyl moiety and the coordination plane around Pd. The bond distances Pd–P 2.340(4) and 2.283(7) Å, as well as, Pd–Cl of 2.346(6) Å in **7c** (values for minor component in Supporting Information) are in agreement with the literature reported distances of 2.306 Å for Pd–P and 2.334 Å for Pd–Cl.[37, 85] The acetylide to palladium distance, Pd–C≡C, is of 1.947(6) Å is also close to reported values of 1.939 Å. The acetylinic bond lengths are of 1.184(8) Å for the Pd coordinated and 1.200(8) Å for the isolated C≡C bonds. These are in accordance to the reported values (1.198 Å)[37, 85] and only slightly shorter when coordinated to the Pd. Finally, the C_{Ar}–O of 1.360(8) Å with the C_{Ar}–O–CH_2 angle of 118.6(5)º are similar to the literature.[37, 85] The coordination around the Pd atoms, viz., the angle values for P–Pd–Cl are of 96.5(2)º and 89.1(2)º with P–Pd–P 171.1(2) and C–Pd–Cl 177.8(2)º, as expected, close to the previously reported values for related systems.[37, 85] Figure 8 shows the packing diagram of complex **7c** (along *a*-axis) where it is possible to observe the layer orientation of the molecules.

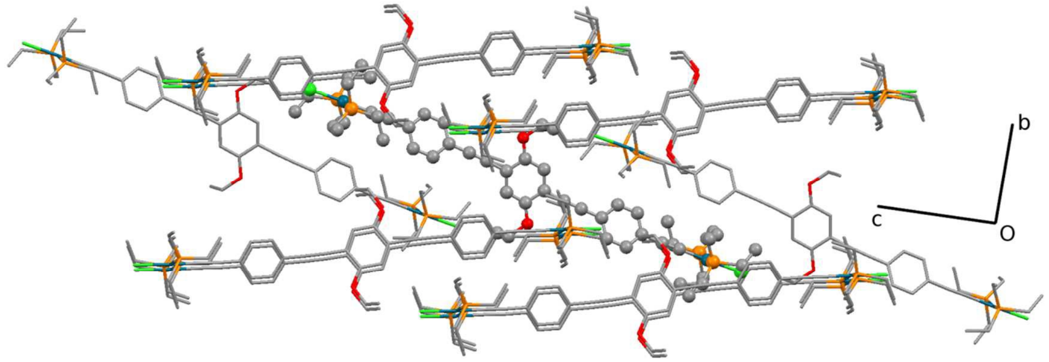


Figure 8. Packing diagram of **7c** (along *a*-axis), which shows the different orientation of the molecules between the layers. The molecule in the asymmetric unit is emphasized (ball-and-stick). The disorder and hydrogen atoms are removed for clarity.

Table 1. Crystallographic data for the structures of 6c and 7c.

	6c	**7c**
CCDC Depository	882324	882325
Crystallization Solvents	CH_2Cl_2/Diethyl ether	CH_2Cl_2/Diethyl ether
Empirical formula	$C_{38}H_{72}Cl_2O_2P_4Pd_2$	$C_{54}H_{80}Cl_2O_2P_4Pd_2$
T (K)	173(2)	123(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.093(2)	13.4614(3)
b (Å)	15.652(3)	11.7059(3)
c (Å)	13.128(3)	18.7397(4)
α (°)	90	90
β (°)	107.02(3)	103.7050(10)
γ (°)	90	90
V (Å^3)	2376.0(8)	2868.89(12)
Z	2	2
ρ_{calc} (g cm^{-3})	1.348	1.353
μ (mm^{-1})	1.032	0.868
Total reflections	19588	9254
Unique reflections	5367	5186
R_{int}	0.1385	0.0292

Crystal size (mm)	0.4 × 0.02 × 0.01	0.13 × 0.6 × 0.06
Colour	Orange	Yellow
Habit	Flat needle	Plate
$F(0\ 0\ 0)$	996	1212
theta$_{min}$ - theta$_{max}$ (°)	3.46 - 27.52	2.34 - 25.25
Data	5367	5186
Restraints	0	421
Parameters	217	424
Goodness-of-fit (GOF) on F^2	1.077	1.055
R indices (all data)		
R_1	0.1425	0.0765
wR_2	0.1003	0.1461
Final R indices ($I > 2\sigma(I)$)		
R_1	0.0709	0.0591
wR_2	0.0814	0.1343
Largest difference in peak and hole (e Å^{-3})	0.658 and -0.711	1.304 and -0.957

Solid-state fluorescence decay studies

Since a potential application of these rods would be as solid-state electronic devices, solid-state fluorescence studies would help to determine the conjugation properties of these materials.[94] We have studied the decay of the fluorescence when the powder samples were excited with a pulsed laser (80 ps pulse width) at 405 nm. The results obtained for the free ligands, and their respective Pd rods are shown in Figure 9 and 10, respectively. The fluorescence decay was detected at about the maximum of the emission bands. A non-exponential decay was observed in all the cases, which is very common for non-diluted solid state samples. The non-exponentially behavior of the decay curves can be due to ligand-to-ligand or ligand-to-metal interactions, as well as to the contribution of a distribution of environments, which is typical in powder samples, The photoluminescence decays are consistent with a multi-exponential equation, which can be useful to estimate an average lifetime that represents the decay rate of the complex[37]. A good agreement was found for a three exponential decay curve (eq. 1).

$$I(t) = B_1 \cdot e^{(-t/\tau_1)} + B_2 \cdot e^{(-t/\tau_2)} + B_3 \cdot e^{(-t/\tau_3)} \qquad (1)$$

The fitting was made using IRF (Instrumental Response Function) reconvolution analysis with F900 software by Edinburgh Instruments. The average lifetime is then calculated using the following equation (eq. 2):[95]

$$\tau_{av} = \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3} \qquad (2)$$

The results for the free ligands and for the Pd complexes are given in Table 3.

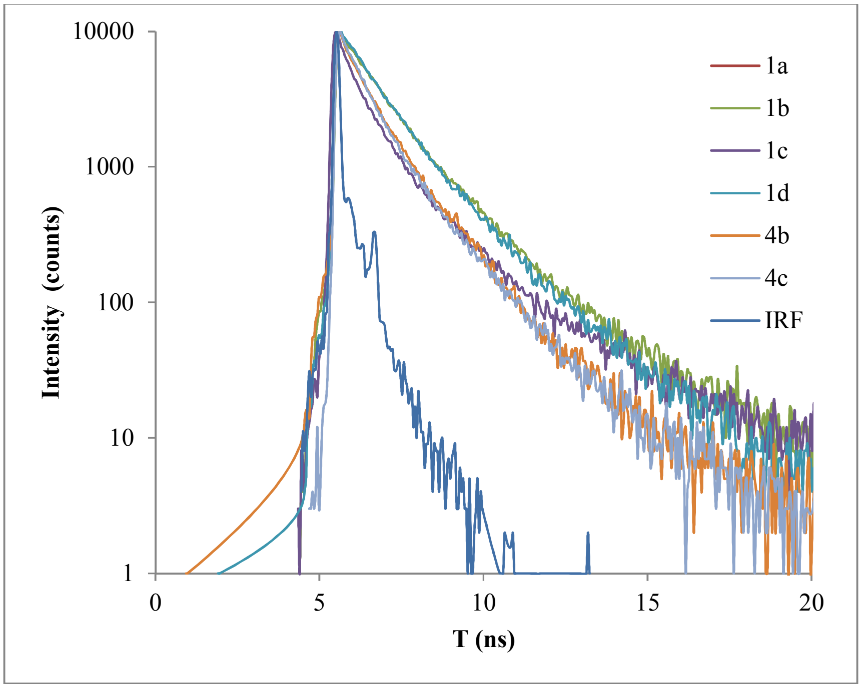


Figure 9. Decay of the fluorescence of the free ligands (**1a-d**, **4b-c**) IRF.

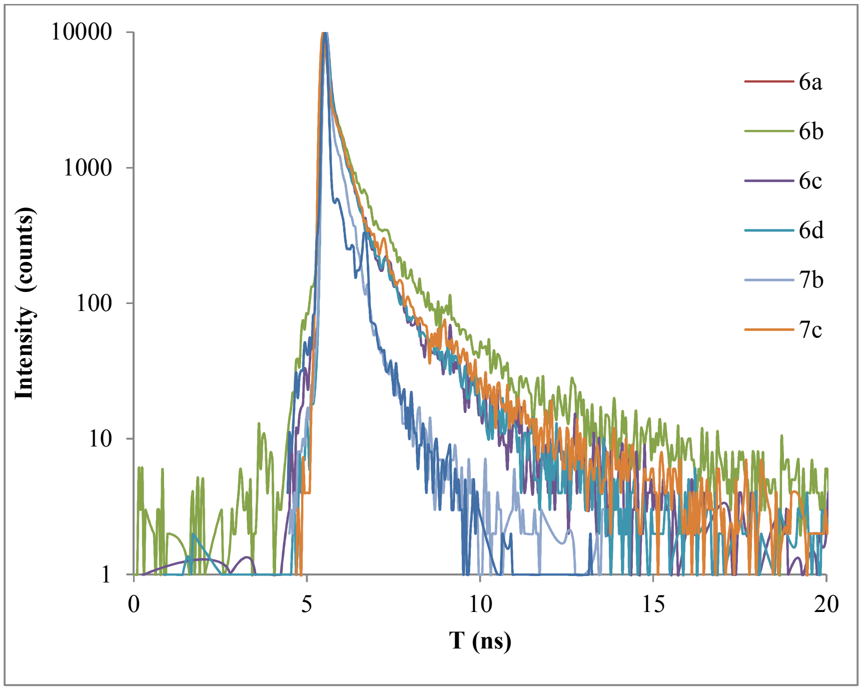


Figure 10. Decay of the fluorescence for the Pd rods (**6a-d**, **7b-c**).

Table 2. Solid-state fluorescence lifetime values for the free ligands (1a-d, 4b-c) and the respective Pd rods (6a-d, 7b-c).

Bridge	λ/nm	τ /ns	Rod	λ/nm	τ /ns
1a	510	0.8	**6a**	454	0.24
1b	510	1.00	**6b**	510	0.60
1c	510	0.70	**6c**	510	0.30
1d	510	0.90	**6d**	510	0.30
4b	510	1.20	**7b**	450	0.05
4c	490	0.95	**7c**	510	0.40

The free ligands (**1a-d**, **4b-c**) show average lifetime values comparable to those found in the literature for the new hybrid composites of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) and clay (montmorillonite), purposely prepared for use in optoelectronic devices (like OLEDs).[96] These nanocomposites show increased lifetimes when the concentration is higher, but values are still on the *pico* second scale. Moreover, lasing capabilities were reported[97] for *p*-

(phenylene ethynylene) polymers, but in solution phase. Nevertheless in the case of small compounds, similar to these presented here, the reported[98] lifetimes values of chloroform solutions of phenylene ethynylenes bearing three rings, values of 2 ns were obtained. Furthermore, this report[98] also shows similar lifetime values for the fluorescence when comparing a tris ringed with its twisted (by a secondary chain) counterpart, even though significantly lower (21 fold) quantum yield was found for the twisted compound. The authors[98] do not account for this discrepancy and attribute it to the equipment's fast decay.

When comparing the values presented in Table 3, higher lifetime values are found for the longer ligands (**4b-c**). Furthermore, a clear trend is observed for all the complexes that were analyzed (**6a-d**, **7b-c**), the average lifetime decreases in the Pd compounds as compared to their respective free ligands. Moreover, a decrease in the emission intensity of the Pd complexes of one or two orders of magnitude was detected when compared to their associated free ligands. This could be accounted by the charge distribution (from ligand to metal centre) reducing available electronic density that would induce a non-radiative relaxation path, which would decrease the lifetime and radiative emission quantum yield.

In particular, for the two compounds for which X-ray data are available, **6c** and **7c**, their average lifetimes can be compared with those of their respective free-ligand molecules, **1c** and **4c**, respectively. In the case of the single ring sample, it reduces from 0.7 ns, in the free ligand **1c** to 0.3 ns for the Pd coordinated complex, **6c**. The lifetime diminishes from 0.95 ns found in the tris ringed free ligand **4c** to 0.4 ns in the corresponding metal complex, **7c**. This represents a similar reduction of lifetime of 43% and 42%, for the single and tris ringed systems. If we consider an important structural parameter obtained from the X-ray analysis, such as the co-planarity angle between the central phenyl and the Pd coordination plane, it changes from 10.96º in the single ring complex, **6c**, to 86.56º for the tris ringed metal compound, **7c**. One could expect a higher overlapping of the π delocalized electronic density to the metal center for a small co-planarity angle. However, the similar lifetime reduction observed in both compounds seems to indicate that a significant ligand to metal charge transfer exists in both cases, despite the low co-planarity exhibited in the **7c** complex. This can be due to the partial tilting between the central and terminal phenyl rings (23.29º), and also to the strong electronegativity of the Pd center.

Experimental section

Materials

Chemicals were used as received unless otherwise noted. All reactions were carried out in dry nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen. Triethylamine and diethylamine, were distilled over potassium hydroxide; *n*-hexane and dichloromethane over calcium hydride; tetrahydrofuran, diethyl ether and toluene over sodium/benzophenone ketyl. Dimethylsulfoxide and glacial acetic acid were used as received and degassed under nitrogen (with stirring or sonication). Methanol was degassed under argon (with sonication). Solvents used in column chromatography were used as received. CuI and CuCl were pre-dried at 120ºC for at least 2 h (usually overnight) before usage. Compound **5**, *trans*-[$PdCl_2(PEt_3)_2$] was used as received from Acros Organics taking care to store it at 4ºC.

Physical measurements

The infra-red spectra were obtained using a Bruker Vertex 70 FTIR spectrophotometer equipped with an ATR (Attenuated total reflectance) diamond add-on. Samples were collected at a resolution of 2 cm^{-1} using a spectral range of 4000 to 400 cm^{-1}. NMR spectra were recorded with a Bruker 400 MHz NMR (Bruker Avance II^+). ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were collected at 400 MHz, 101 MHz and 161 MHz respectively. The chemical shifts (δ) are reported in ppm and referenced to residual solvent peaks[99] for ^1H and ^{13}C. ^{31}P NMR is referenced to external 85% H_3PO_4. Melting points were determined with an Electrothermal 9200 Melting point apparatus, using sealed capillaries without calibration. Mass spectra were obtained using a Micro-mass LCT spectrometer ESI-TOF spectrometer. Elemental analyses were carried out by using a VariolEL instrument from Elementar Analysensysteme. Cyclic voltammetry was performed using a PARSAT advanced electrochemical equipment with tetra-*N*-buthylamonium hexafluorophosphate 0.1 M as supporting electrolyte in CH_2Cl_2 with analyte concentration of $1x10^{-3}$ M. The reference electrode used was the Ag/AgCl (saturated KCl). Platinum was used as the working and secondary electrodes. The potentials were calibrated against the ferrocene/ferrocenium couple. Absorption spectra were recorded using a GBC-Cintra

40 in dry and degassed (argon) CH_2Cl_2 at $1x10^{-5}$ M for the free ligands (**1a-d**, **4b-c**) and *trans*-$[PdCl_2(PEt_3)_2]$ (**5**) and at $1x10^{-6}$ M for the rods (**6a-d**, **7b-c**). All solution measurements were performed using dry and degassed solvent and at room temperature unless otherwise noted. Lifetime fluorescence studies were carried out by measuring the samples in the form of powder between two microscope slides. The measurements were then performed using LifeSpec II Spectrometer from Edinburg Instruments, with a pulsed 405 nm diode laser with 80 ps pulse duration as the excitation source. The Instrumental Function Response (IRF) of the spectrometer has been measured in order to correct the lifetime data. As the powders samples did not present all the same particle size and sample size was different, integrated fluorescence spectra can only be compared by orders of magnitude of difference. Accordingly, samples are compared to their average lifetimes, which is independent of the factors referred above.

Synthesis of the bridging ligands

The new 1,4-diethynylbenzene single ringed derivatives (Scheme 1), were prepared according methods previously described in the literature (**1a**,[34] **1b**[63] and **1c-d**[62]). The longer bridging ligands (**4b-c**) were prepared following the Sonogashira-Hagihara procedures[19, 41, 62, 65-69] by coupling the shorter analogues (**1b-c**, respectively) with 1-iodo-4-bromobenzene followed by another coupling to insert the terminal acetylenic moiety (Scheme 3). Cleavage of the trimethylsilyl protecting group was achieved with KF, or K_2CO_3.[100] The preparation of the intermediaries (**2b-c**, **3b-c**) is detailed in the Supplementary Information.

1,4-dimethoxy-2,5-bis((4-ethynylphenyl)ethynyl)benzene, 4b

1,4-dimethoxy-2,5-bis((4-trimethylsilylethynylphenyl)ethynyl)benzene (**3b**, 350 mg, 0.65 mmol) was dissolved in CH_2Cl_2/MeOH (60 mL, 1:1) and K_2CO_3 (211 mg, 1.52 mmol) was added in one portion. The reaction mixture was stirred for 16 h at room temperature and then filtrated. The resulting solution was evaporated under low pressure and purified by column chromatography (neutral alumina, petroleum ether (40-60 ºC) and 5% diethyl ether). Compound **4b** was obtained as a yellow powder (200 mg, 58.8 %). Mp = 170-172 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 3.18 (*s*, 2H, C≡C-*H*), 3.91 (*s*, 6H, OCH_3), 7.03 (*s*, Ar-*H*, central ring) 7.47 (*d*, 4H, Ar-*H* outer ring, $J_{H,H}$= 8.20 Hz), 7.52 (*d*, 4H, Ar-*H* outer ring, $J_{H,H}$ = 8.28 Hz). $^{13}C\{^1H\}$ NMR (101

MHz, $CDCl_3$): *δ* 56.9 (*s*, O*C*H_3), 79.3, 83.7, 88.0, 94.9 (*s*, C≡C, internal and external), 113.8, 116.0, 122.4, 124.1, 131.9, 132.4 (*s*, Ar. central and outer rings), 154.4 (*s*, Ar. *C*–O–CH_3). FTIR (cm^{-1}): $\tilde{\nu}$ = 3271 (m, $\nu_{C\equiv C\text{-}H}$), 2102 (vw, $\nu_{C\equiv C}$), 655 (s, $\delta_{C\equiv C\text{-}H}$), 1510 (w), 1500 (w), 1491.79 (w), 1461 (w), 1936 (m) (ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{28}H_{18}O_2$: *m/z* = calc. 409.12, found 409.12 $[M+Na]^+$; calc. 441.15, found 441.13 $[M+Na+CH_3OH]^+$; calc. 493.10, found 493.13 $[M+K+Cl+CH_3OH+H]^+$; calc. 795.25, found 795.23 $[2M+Na]^+$. Anal. Calcd. for $C_{28}H_{18}O_2·2H_2O$ (422.48): C, 79.60; H, 5.25 found C, 66.5; H, 5.17.

1,4-diethoxy-2,5-bis((4-ethynylphenyl)ethynyl)benzene, 4c

Following the same conditions as described for **4b**, 1,4-diethoxy-2,5-bis((4-trimethylsilylethynylphenyl)ethynyl)benzene (**3c**, 25 mg, 0.44 mmol) was dissolved in CH_2Cl_2/MeOH (50 mL, 1:1) and K_2CO_3 (15 mg, 0.10 mmol) was added at once. The reaction mixture was stirred for 16 h at room temperature and then filtrated. The final solution was evaporated under low pressure and purified by column chromatography (neutral alumina, petroleum ether (40-60 ºC) and 5% diethyl ether). The target compound **4c** as obtained as a yellow powder (14 mg, 75.5 %). Mp = 212-215 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 1.48 (t, 6H, $J_{H,H}$ =6.97 Hz), 3.17 (s, 2H, C≡C-*H*), 4.11 (s, 6H, OC*H_3*), 7.01 (s, Ar-*H*, central ring), 7.47 (d, 4H, Ar-*H* outer ring, $J_{H,H}$ =8.56 Hz), 7.49 (d, 4H, Ar-*H* outer ring, $J_{H,H}$ =8.60 Hz).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 15.1 (s, OCH_2CH_3), 65.5 (s, OCH_2CH_3), 79.1, 83.5, 88.1, 94.6 (s, C≡C, internal and external) 117.4, 122.1, 124.1, 131.6, 132.2 (s, Ar. central and outer rings), 153.7 (s, Ar. *C*–O–CH_2CH_3). FTIR (cm^{-1}): $\tilde{\nu}$ = 3275 (m, $\nu_{C\equiv C\text{-}H}$), 2105 (vw, $\nu_{C\equiv C}$), 661 (s, $\delta_{C\equiv C\text{-}H}$), 1516 (m), 1499 (w), 1489 (w), 1474 (w), 1417 (m), 1403 (m), 1392 (m) (ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{30}H_{22}O_2$: *m/z* = calc. 437.15, found 437.20 $[M+Na]^+$; calc. 469.18, found 469.22 $[M+Na+CH_3OH]^+$; calc. 851.31, found 851.37 $[2M+Na]^+$. Anal. Calcd. for $C_{30}H_{22}O_2·0.45\ H_2O$ (422.2): C, 85.26; H, 5.46; found C, 85.2; H, 5.56.

Synthesis of the palladium complexes

The bridged palladium complexes (Scheme 1) were obtained modifying the method reported by Onitsuka[40], coordinating the described ligands (**1a**-**d**, **4b-c**) to the *trans*-$[PdCl_2(PEt_3)_2]$ (**5**) moiety in diethylamine (solvent and base) using copper (I) (CuCl 5% molar eq.) as a catalyst.

1,4-bis[*trans*-$(PEt_3)_2ClPd–C≡C$]benzene, 6a

Compound 1,4-bis[*trans*-$(PEt_3)_2ClPd–C≡C$]benzene **(6a)**, was first prepared by us, but, Mukherjee and co-workers[85] were able to publish previously its preparation, with only minor differences. For that reason and because its preparation was confirmed by FTIR, NMR and MS spectroscopy, no EA analysis was performed in that case. Compound **6a** is prepared, in the same way, as the other short Pd rods (**6b-d**). Briefly, the starting material *trans*-$[PdCl_2(PEt_3)_2]$ (**5**, 200 mg, 0.48 mmol) and **1a** (41 mg, 0.32 mmol) were dissolved in $NHEt_2$ (20 mL). CuCl (1 mg, 0.01 mmol) was added in one portion and the mix was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. A yellow powder was obtained (142 mg, 49.6 %). Mp = 119 ºC (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ 1.51 (t, *J* = 21Hz, 36H, $PCH_2–CH_3$), 1.92 (q, *J* = 8Hz, 24H, PCH_2), 7.07 (s, 4H, Ar-*H*). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): δ 8.3 (PCH_2CH_3), 15.4 (vt, *J* C-P= 13.80Hz, PCH_2CH_3), 125.1, 130.4; $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.1. FTIR (cm^{-1}): $\tilde{\nu}$ = 2118 (w, νC≡C); 1498 (m), 1452 (m), 1409 (m), 1378 (m) (ar. νC=C). TOF-MS (ESI+) of $C_{34}H_{64}Cl_2P_4Pd_2$: *m/z* = calc. 727.1, found 727.0 $[M\text{-}Cl\text{-}PEt_3+H]^+$, calc. 845.2 , found 845.1 [M-Cl]+, 903.1 $[M+Na]^+$.

1,4-bis[*trans*-$(PEt_3)_2ClPd–C≡C$]-2,5-dimethoxybenzene, 6b

The starting material *trans*-$[PdCl_2(PEt_3)_2]$ (**5**, 200 mg, 0.48 mmol) and **1b** (40 mg, 0.12 mmol) were dissolved in $NHEt_2$ (20 mL). CuCl (1 mg, 0.01 mmol) was added in one portion and the mixture was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. Complex **6b** was obtained as a yellow powder (128 mg, 62.9 %). Mp = 153 ºC (decomp.) ^1H NMR (400 MHz,

$CDCl_3$): δ 1.21 (t, J = 21Hz, 36H, PCH_2–CH_3), 2.02 (q, J = 8Hz, 24H, PCH_2), 3.75 (s, OCH_3), 6.69 (s, 2H, Ar–H).$^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): δ 8.0 (PCH_2CH_3), 15.3 (t, $J_{C–P}$= 13.80Hz, PCH_2CH_3), 30.9 (Pd–C≡C), 42.2 (Pd–C≡C), 56.2 (C_1), 115.7 (C_3), 154.3 (C_2). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.1. FTIR (cm^{-1}): $\tilde{\nu}$ = 2115 (s, $\nu_{C≡C}$), 1493 (m), 1454 (m), 1409 (m), 1385 (m) (ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{36}H_{68}O_2Cl_2P_4Pd_2$: m/z = 907.21, found 907.70 $[M\text{-}Cl+2H]^+$; calc. 963.15, found 963.09 $[M+Na]^+$. Anal. Calcd. for $C_{36}H_{68}Cl_2O_2P_4Pd_2 \cdot 1.05H_2O$ (969.46) C, 45.07; H, 7.36; found C, 44.74; H, 7.03.

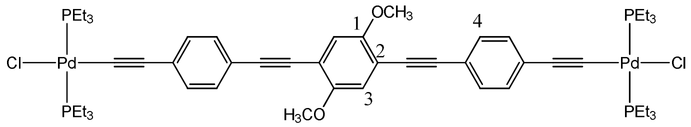
1,4-bis[*trans*-(PEt$_3$)$_2$ClPd– C≡C]-2,5-diethoxybenzene, 6c

The starting material *trans*-[$PdCl_2(PEt_3)_2$] (**5**, 250 mg, 0.60 mmol) and **1c** (58 mg, 0.27 mmol) were dissolved in $NHEt_2$ (20 mL). CuCl (1 mg, 0.01 mmol) was added in one portion, and the mixture was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. The final product was obtained as a yellow powder (214 mg, 76.3 %). Orange crystals were obtained by diffusion of diethyl ether in a saturated dichloromethane solution at -20ºC. Mp = 145 ºC (decomp.) ^1H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, J = 20Hz, 36H, PCH_2–CH_3), 1.46 (t, J = 18Hz, 6H, OCH_2–CH_3), 2.01 (q, J = 18Hz, 24H, PCH_2), 3.97 (q, J = 18Hz, 4H, OCH_2), 6.69 (s, 2H, Ar–H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 8.7 (PCH_2CH_3), 15.5 (s, OCH_2CH_3), 15,7 (t, $J_{C–P}$= 13.97Hz, PCH_2CH_3), 64.8 (s, OCH_2CH_3), 100.1 (t, $J_{C–P}$ = 16.06 Hz, Pd–C≡C), 102.9 (t, $J_{C\text{-}P}$ = 5.83 Hz, Pd–C≡C), 116.0 (s, C_1), 117.4 (s, Ar.), 153.2 (s, Ar. C–O–CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.0. FTIR (cm^{-1}): $\tilde{\nu}$ = 2113 (w, $\nu_{C≡C}$), 1498 (m), 1478 (m), 1409 (m), 1389 (m, ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{38}H_{72}Cl_2O_2P_4Pd_2$: m/z = calc. 933.24, found 933.14 $[M\text{-}Cl+H]^+$; calc. 991.18, found 991.10 $[M+Na]^+$. Anal. Calcd. for $C_{38}H_{72}Cl_2O_2P_4Pd_2 \cdot 0.75CH_2Cl_2 \cdot 0.35H_2O$ (1038.59): C, 44.81; H, 7.20; found: C, 44.85; H, 7.24.

1,4-bis[*trans*-(PEt$_3$)$_2$ClPd–C≡C]-2,5-dihepthoxybenzene, 6d

The starting material *trans*-[$PdCl_2(PEt_3)_2$] (**5**, 250 mg, 0.60 mmol) and **1d** (96 mg, 0.27 mmol) were dissolved in $NHEt_2$ (20 mL). CuCl (1 mg, 0.01 mmol) was added in one portion and the mixture was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. Compound **6d** was obtained as a yellow powder (193 mg, 62.5 %). Mp = 98.9 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J= 6.86 Hz, 6H, $O(CH_2)_6C\mathit{H}_3$)), 1.19−1.31 (m, 52H, $PCH_2–C\mathit{H}_3$, $O(CH_2)_2(C\mathit{H}_2)_4CH_3$), 1.48–1.93 (m, $OCH_2C\mathit{H}_2(CH_2)_4CH_3$), 3.89 (t, *J*=6.82 Hz, 4H, $OC\mathit{H}_2(CH_2)_5CH_3$), 2.03 (q, *J* = 7.4Hz, 24H, $PC\mathit{H}_2$), 6.69 (s, 2H, Ar–*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 8.0 ($PCH_2\mathit{C}H_3$), 15.3 (t, $J_{\text{C-P}}$= 13.80Hz, $P\mathit{C}H_2CH_3$), 5.7, 13.8, 22.6, 26.1, 29.2, 29.7, 31.8 ($(OCH_2)_6CH_3$), 99.6 (s, Pd-*C*≡C, $J_{\text{C-P}}$ = 16.13Hz), 102.7 (Pd-C≡*C*, $J_{\text{C-P}}$ = 5.50Hz), 115.6, 117.1 (s, Ar. *C*), 152.8 (s, Ar. *C*–O–CH_2). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.5. FTIR (cm^{-1}): $\tilde{\nu}$ = 2113 (w, $\nu_{C\equiv C}$), 1498 (m), 1478 (m), 1404 (m), 1389 (m) (ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{48}H_{92}Cl_2O_2P_4Pd_2$: *m/z* = calc. 1131.34, found 1131.34 $[M+Na]^+$; calc. 2240.69, found 2240.51 $[2M+Na+H]^+$; Anal. Calcd. for $C_{48}H_{92}Cl_2O_2P_4Pd_2{\cdot}2H_2O{\cdot}0.6CH_2Cl_2$ (1192.74): C, 48.81; H, 8.19; found: C, 48.83; H, 8.21.

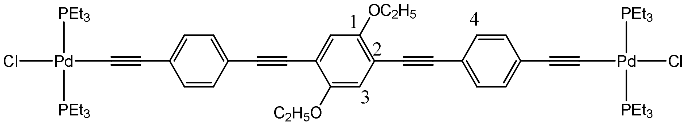
1,4-bis[*trans*-$(PEt_3)_2ClPd$-4-($C\equiv C–C_6H_4–C\equiv C$)]-2,5-dimethoxybenzene, 7b



The starting material *trans*-$[PdCl_2(PEt_3)_2]$ (**5**, 300 mg, 0.72 mmol) and **4b** (126 mg, 0.32 mmol) were dissolved in $NHEt_2$ (40 mL). CuCl (1 mg, 0.01 mmol) was added at once and the mixture was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure, giving **7b** as a yellow powder (273 mg, 74.4 %). Mp = 155 ºC (decomp.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, *J* = 8.18Hz, 36H, $PCH_2—C\mathit{H}_3$), 1.98 (q, *J* = 3.61Hz, 24H, $PC\mathit{H}_2$), 3.90 (s, 6H, $OC\mathit{H}_3$), 7.01 (s, 2H, Ar-*H*), 7.21 (d, 4H, $^3J_{H,H}$ = 8.08 Hz), 7.42 (d, 4H, $^3J_{H,H}$ = 8.12 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 8.7 (s, $PCH_2\mathit{C}H_3$), 15.8 (t, $J_{\text{C-P}}$= 13.97 Hz, $P\mathit{C}H_2CH_3$), 56.7 (s, $O\mathit{C}H_3$), 86.8, 95.8 (s, C≡C, internal), 99.5 (t, Pd-C≡*C, J* $_{\text{C-P}}$ = 16.13Hz), 107.1 (t, Pd-*C*≡C*, J* $_{\text{C-P}}$ = 5.87Hz), 113.9, 116.0, 120.5, 128.3, 130.9 (s, Ar. central and outer rings), 154.3 (s, Ar. *C*–O–CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.4. FTIR (cm^{-1}): $\tilde{\nu}$ = 2110 (w, $\nu_{C\equiv C}$), 1501 (m), 1488 (m), 1457 (m), 1397 (m) (ar.

$\nu_{C=C}$). TOF-MS (ESI+) of $C_{54}H_{80}Cl_2O_2P_4Pd_2$: *m/z* = calc. 763.19, found 763.19 $[M\text{-}(PdCl(PEt_3)_2)+H]^+$; calc. 881.22, found 881.26 $[M\text{-}(PdCl(PEt_3)_2)+H+PEt_3]^+$; calc. 987.18, found 987.15 $[M\text{-}Cl\text{-}PEt_3+H]^+$; calc. 1105.26, found 1105.26 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{52}H_{76}Cl_2O_2P_4Pd_2 \cdot 0.35H_2O$ (1147.09) C, 54.45; H, 6.74; found: C, 54.33; H, 6.59.

1,4-bis[*trans*-(PEt$_3$)$_2$ClPd-4-(C≡C–C$_6$H$_4$–C≡C)]-2,5-diethoxybenzene, 7c



The starting material *trans*-$[PdCl_2(PEt_3)_2]$ (**5**, 250 mg, 0.60 mmol), and **4c** (100 mg, 0.24 mmol) were dissolved in $NHEt_2$ (30 mL). CuCl (1 mg, 0.01 mmol) was added in one portion and the mixture was stirred at room temperature for 14 h. It was then evaporated and redissolved in CH_2Cl_2. The resulting solution was washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. The target compound **7c** was obtained as a yellow powder (241 mg, 85.9 %). Yellow crystals were obtained by diffusion of diethyl ether in a saturated dichloromethane solution at -20ºC. Mp = 150 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, *J* = 8.02Hz, 36H, PCH_2—CH_3), 1.48 (t, 6H, OCH_2CH_3) 1.98 (q, *J* = 3.61Hz, 24H, PCH_2), 4.10 (s, 4H, OCH_2CH_3), 6.95 (s, 2H, Ar-*H*), 7.21 (d, 4H, $^3J_{H,H}$ = 8.44 Hz), 7.40 (d, 4H, $^3J_{H,H}$ = 8.44 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 8.7 (s, PCH_2CH_3), 15.3 (s, OCH_2CH_3) 15.8 (t, $J_{C\text{-}P}$= 1393 Hz, PCH_2CH_3), 5.7 (s, OCH_3), 87.1, 95.6 (s, C≡C, internal), 99.4 (t, Pd-C≡*C*, $J_{C\text{-}P}$ = 15.80Hz), 107.1 (t, Pd-*C*≡C, $J_{C\text{-}P}$ = 5.53Hz), 114.6, 117.6, 120.5, 128.2, 130.9 (s, Ar. central and outer rings), 153.8 (s, Ar. *C*–O–CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 18.1 ppm. FTIR (cm^{-1}): $\tilde{\nu}$ = 2112 (w, $\nu_{C\equiv C}$), 1510 (m), 1487 (m), 1454 (m), 1413 (m) 1377 (m) (ar. $\nu_{C=C}$). TOF-MS (ESI+) of $C_{54}H_{80}Cl_2O_2P_4Pd_2$: *m/z* = calc. 1133.29 found 1133.33 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{54}H_{80}Cl_2O_2P_4Pd_2$ (1168.83): C, 55.49; H, 6.90; found: C, 56.10; H, 6.74.

Crystallographic data collection and structure determination

X-ray data for compounds **6c** and **7c**, was collected using a Bruker-Nonius KappaCCD difractometer with APEX-II detector at 173(2) and 123(2) K, respectively, using MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods with SIR-2004[101] and refined by least squares using SHELXL-97.[102] Hydrogen atoms were included at calculated positions and refined as riding atoms with isotropic displacement parameters coupled to those of the parent atoms. The non-hydrogen atoms were refined using anisotropic parameters. ORTEP-3[83] plots have been drawn with 30% probability ellipsoids. For disordered **7c,** a large number of restraints were applied to stabilize the structure of major and minor components. The Pd−Cl, Pd−P and P−C bond distances were restrained to be equal (s = 0.02) in both components. Also, all C−C distances in ethyl groups bonded to P atoms, as well as, all P−methyl distances over two bonds were restrained to be equal (s = 0.02). Anisotropic displacement parameters for Cl, P and disordered C atoms were restrained to be equal (s = 0.01 for P and methylene C, s = 0.02 for Cl and methyl C). Furthermore, two atoms of the minor component were restrained to show more isotropic shape (s = 0.01).

Conclusions

The design and synthesis of novel molecular non-metallated or metallated systems is a hot topic of current research, since the potential integration of these functional molecular structures within electronic devices could extend the life of silicon technology. In this work, we have reported the preparation, structural characterization and electrochemical properties of a rare family of $[PdCl(PEt_3)_2]^+$ rods based on derivatives of 1,4-diethynylbenzene (phenylene ethynylene rods with alkoxy side chains; methoxy, ethoxy and heptoxy). It was also systematically studied, the effect of substituents attached to bridging ligands on the electronic communication between the two metal centers and, on the solid-state photoluminescence efficiency on these family of binuclear $[PdCl(PEt_3)_2]$ phenylene ethynylene rods. Preparation of bridging ligands was done using Sonogashira-Hagira coupling, and two new ligands (**4b-c**) were obtained in good yields as well as the resulting bimetallic rods. The structures of

1,4-bis[*trans*-$(PEt_3)_2$ClPd–C≡C]-2,5-diethoxybenzene (**6c**) and the longer rod 1,4-bis[*trans*-$(PEt_3)_2$ClPd-4-(–C≡C–C_6H_4–C≡C)]-2,5-diethoxybenzene (**7c**) were unambiguously confirmed by single crystal X-ray crystallography. Although the usage of the side chains does permit better manipulation (solubility) of the materials and, induces lower oxidation potentials in regards to the undecorated rods, our results show no significant differences as the length of these chains increases. It was observed that the increase of the length of the new bridging ligands brings about a higher oxidation potential in relation to the shorter counterparts. Fluorescence lifetime values are found to be longer in the ligands (**4b-c**) than in the studied Pd complexes (**6a-d**, **7b-c**), which exhibit a marked decrease in both the emission intensity and in the fluorescence lifetime values. This observation could be due to some degree of ligand to metal charge transfer. Based in current results, the development of new hybrid molecular/semiconductor systems formed by non-metallated or metallated π-conjugated oligo(phenylene ethynylene)s molecular wires, covalently grafted onto non previously functionalized porous silicon substrates are currently underway in our laboratory, having in view their possible application as waveguides.

Associated content

Electronic Supporting Information

^{1}H, ^{13}C, ^{31}P NMR, FTIR and UV-Vis spectra as well the remainder of the cyclic voltammograms can be found in the Supplementary Information. This material is available free of charge via the Internet at: http://pubs.rsc.org. CCDC 882324 and 882325 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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Notes

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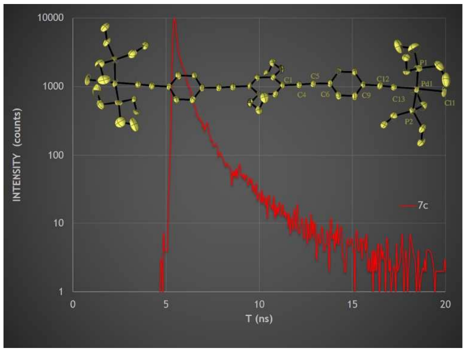
Graphical Abstract



Textual Abstract

Six rare binuclear [PdCl(PEt$_3$)$_2$] phenylene ethynylene rods with alkoxy side chains have been prepared. Solid-state photoluminescence studies revealed a decrease in the emission intensity when moving from the free ligands to the Pd complexes.