Dalton Transactions

PAPER

RSC Publishing

View Article Online View Journal

Cite this: DOI: 10.1039/c3dt32843k

Received 27th November 2012, Accepted 9th January 2013 DOI: 10.1039/c3dt32843k

www.rsc.org/dalton

Introduction

For years several groups have shown the advantages of fluorinated aryl ligands to isolate and study organometallic complexes of transition metals, such as Pt or Pd,¹ Ag,² and Au.³ In general, M–aryl bonds are weaker and more reactive ligands than the analogous M–fluoroaryl bonds. The higher polarity of the latter M–C bond contributes to its higher strength and

Highly fluorescent complexes with gold, palladium or platinum linked to perylene through a tetrafluorophenyl group†

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Treatment of 3-(1-hexynyl)perylene with Co₂(CO)₈ resulted in the formation of the dinuclear cobalt complex $[Co_2(CO)_6(\mu-\eta^2-C_4H_9C\equiv C-Per)]$ (Per = 3-perylenyl) (1). The perylene derivatives 3-(2,3,5,6-tetrafluorophenyl)perylene (PerC₆F₄H) and 3-(2,3,5,6-tetrafluorophenyl)-9(10)hexylperylene (C₆-PerC₆F₄H) were prepared and used to synthesize $[AuR(CN^tBu)]$ (R = PerC₆F₄ 2a), $[AuR(CN(C_6H_2)-3,4,5-(OC_{12}H_{25})_3)]$ (R = $PerC_6F_4$ (**3a**), $R = C_6-PerC_6F_4$ (**3b**)), trans-[PdR(PR'_3)_2X] ($R = PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, $R' = PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, $R' = PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, $R' = PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, $R' = PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph, X = I (**4a**)); ($R = C_6-PerC_6F_4$, R' = Ph) ($R = C_6-PerC_6F_4$); ($R = C_6-Pe$ R' = Ph, X = I (4b)); (R = PerC₆F₄, R' = Et, X = I (5a)); (R = C₆-PerC₆F₄, R' = Et, X = I (5b)); (R = PerC₆F₄ Ph, X = NCS (**6a**)), and trans-[Pd(PerC₆F₄)(PEt₃)₂X] (X = Br (**7a**); X = I (**8a**)). The molecular structure of complexes 1, 2a, and 6a has been determined by X-ray diffraction analysis. The perylenyl fragments of complexes 2a or 6a are essentially planar and make dihedral angles to the tetrafluorophenyl plane of 57.49° (2a) and 77.75° (6a). No π - π stacking of perylenyl rings is observed in any of the three molecules, but 2a shows association of two monomers (arranged almost antiparallel), with an Au…Au distance of 3.114 Å. DFT calculations were performed on the absorption spectra of representative $PerC_6F_4Y$ (Y = H, F, Au(CNMe), PtBr(PMe₃)₂ and PdBr(PMe₃)₂). All complexes exhibit fluorescence associated with the perylene fragment with emission quantum yields, in solution at room temperature, in the range 0.20-0.90 and emission lifetimes ~4 ns, and no significant differences in the emission maxima, due to an efficient electronic decoupling of the metal fragment from the HOMO and LUMO of the perylene chromophore. The latter is confirmed by DFT calculations.

> inertness. Fluoroaryls are also better π -acceptors when bonded to suitable electron-rich metal centers. The result is that fluoroaryls allow for isolation of stable organometallic complexes, including some, otherwise difficult to observe, intermediates in important catalytic processes.⁴

> We have recently reported platinum organometallic complexes of perylene with Pt directly σ -bonded to the 3 position of the perylene core, and studied how the coordination of platinum affects the photophysical properties of the material.⁵ It was found that the coordination of Pt has only a moderate quenching effect on the fluorescence (these organoplatinum complexes show intense fluorescence, about 70–80% that of the mother organic molecule), in spite of the fact that directly attaching metal centers to aromatic cores of organic chromopheres is often very detrimental for fluorescence.^{6,7}

Frequently, the optical properties are noticeably modified upon changing the metals in the material. We wanted to know the effect of replacing Pt by Pd or Au in a common perylene skeleton, but the direct bonds of Pd or Au to perylene are not stable enough to isolate the corresponding complexes, study their optical properties, and compare them with the Pt complexes. Thus, we decided to obtain perylene derivatives with

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[†]Electronic supplementary information (ESI) available: Selected interatomic distances (Å) and angles (°) for the second molecule of complex **1** and a view of the two different molecules of **1**, absorption and emission spectra of **8** in different solvents, cyclic voltammogram of compounds **2a**, **4a** and **4b**, fluorescence decays for **4a** and **4b**, calculated absorption spectra parameters for PerC₆F₄-Y compounds (in gas phase and chloroform solution), and schematic representation of the main electronic transitions expected in the absorption spectra for PerC₆F₄MBr(PMe₃)₂ with M = Pd or Pt. CCDC 870559, 870560, 870561. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32843k

gold, palladium or platinum attached to perylene through a tetrafluorophenyl link, by functionalizing the perylene molecule with a tetrafluorophenyl group and submitting it to metallation with Au, Pd or Pt moieties. The presence of the $C_6F_4ML_n$ substituent (M = Au, Pd, Pt) could be an efficient entry to new structural and functional motifs, significantly widening the diversity of photofunctional systems available. As discussed below, the C_6F_4 link turned out to be rather efficient to electronically disconnect the ML_n from the perylenyl fragment.

Since a problem in the study of perylene derivatives is the poor solubility of the compounds, our strategy also included enhancing the solubility by incorporating appropriate ligands to the metal center. An additional strategy for solubilization has been to attach an alkyl (hexyl) substituent on the perylene core. This second strategy is more synthetically demanding, and leads to mixtures of isomers. Gold(1), palladium(11) and platinum(11) complexes with the tetrafluorophenylperylenyl and C6-tetrafluorophenylperylenyl fragments have been prepared. Since 3-(1-hexynyl)perylene was an intermediate in the synthesis of C₆-tetrafluorophenylperylene, it was used to prepare another structural type, the corresponding [Co₂(CO)₆(μ - η^2 -C₄H₉C=C-Per)] (Per = 3-perylenyl).

Results and discussion

Synthesis and characterization

3-(1-Hexynyl)perylene was prepared by a Sonogashira coupling of 3-bromoperylene with 1-hexine, following a similar literature procedure.⁸ Treatment of 3-(1-hexynyl)perylene with $Co_2(CO)_8$ in dichloromethane at room temperature, for 2 h, resulted in the formation of the dinuclear Co complex 1 (Scheme 1). This dark olive green complex is soluble in organic solvents such as chloroform, dichloromethane, toluene, acetone and THF, but insoluble in hexane or alcohols.



 $\label{eq:scheme1} \begin{array}{lll} \mbox{(i)} \ \mbox{Pd}(OAc)_2 \ (5 \ \mbox{mol}\%), \ \mbox{P}^t Bu Me-HBF_4 \ (10 \ \mbox{mol}\%), \ \mbox{K}_2 CO_3 \ (1.1 \ \mbox{equiv.}), \ \mbox{DMA}, \ 120 \ \ \mbox{°C; (ii)} \ 1-hexyne, \ \mbox{Pd}_2 dba_3, \ \mbox{PPh}_3, \ \mbox{Cul.} \end{array}$

The IR spectrum shows three strong absorptions at 2086, 2050 and 2022 cm⁻¹ for the terminal carbonyl groups, in the expected range for similar η^2 -alkyne adducts containing a Co₂(CO)₆ fragment.^{9,10} The ¹H NMR spectrum of **1** in CDCl₃ shows deshielding of the signals of the C α C-CH₂ group (3.32 ppm) as compared with 3-(1-hexynyl)perylene (2.60 ppm). The structure of **1** was unequivocally confirmed by X-ray crystallography (see below).

The hydrogenation of 3-(1-hexynyl)perylene in THF yielded 3-hexylperylene quantitatively. Following a literature procedure,¹¹ 3-hexylperylene was brominated with NBS in DMF to yield a 1:1 mixture of isomers 3-bromo-9-hexyl- and 3-bromo-10-hexylperylene, which could not be separated.

Coupling of 3-bromoperylene with tetrafluorophenylboronic acid, following a literature procedure for highly inactive fluorophenylboronic acids,¹² produced very low yield (5%) of 3-(2,3,5,6-tetrafluorophenyl)perylene (PerC₆F₄H). Much more effective was a procedure described for intermolecular direct arylation of electron-deficient arenes,¹³ which yielded more than 50% of the coupling product PerC₆F₄H, impurified with 3-5% of perylene, as a yellow solid. Identical conditions were used to obtain a mixture of isomers 3-tetrafluorophenyl-9-hexylperylene and 3-tetrafluorophenyl-10-hexylperylene (C₆-PerC₆F₄H) as a yellow solid, clearly more soluble in common organic solvents than PerC₆F₄H.

The ¹H NMR spectrum of PerC₆F₄H shows the signal of C₆F₄H as a multiplet at 7.21 ppm, whereas the ¹⁹F NMR spectrum displays two sets of multiplets (AA'XX'Z spin system) at –139.1 and –140.2 ppm. The aromatic region in the ¹H NMR spectrum of C₆-PerC₆F₄H is complex because of the presence of the two substitutional isomers; in addition, it displays a multiplet at 7.38 ppm for C₆F₄H, and the signals of the alkyl chain attached to perylene: one triplet at 3.05 ppm for the *CH*₂ group bonded directly to perylene, and the remaining alkyl chain H atoms as unresolved signals in the range 0.8–1.8 ppm. As expected, the ¹⁹F NMR spectrum is very similar to that of PerC₆F₄H.

The bromo or iodo derivatives of R-PerC₆F₄H (R = H, C₆) were obtained by treating a solution of R-PerC₆F₄H, in THF at -70 °C, with BuLi, and subsequently adding Br₂ or I₂, respectively (Scheme 2). The compounds obtained were contaminated with perylene (<5%), but were used as such in the subsequent reactions with metal centers, as it is easier to purify the complexes than the precursor. As expected, the ¹H NMR spectra of the complexes showed the disappearance of the proton of the fluoroaromatic group, and the ¹⁹F NMR spectra displayed AA' XX' spin system for the C₆F₄X moiety, with two groups of signals corresponding to the F_{ortho} and the F_{meta} atoms.

The gold(i) isocyanide complexes **2a** and **3a,b** were obtained in two steps by arylation of [AuCl(tht)] followed by ligand exchange with isocyanide. Their IR spectra show one ν (C \equiv N) absorption at 2226 cm⁻¹ for **2a**, and at 2213 cm⁻¹ for **3a,b**, at higher wavenumbers than for the free isocyanide, as an effect of coordination to gold(i).^{3a,14} The ¹H NMR spectra of the gold(i) isocyanide complexes show the signals of the corresponding isocyanide, and the ¹⁹F NMR spectra show two



 $\label{eq:scheme 2} \textbf{(i) 1. BuLi; 2. ClAu(tht); (ii) 1. BuLi; 2. X_2.}$

complex multiplets corresponding to an AA'XX' system. Complexes **3a,b** were hoped to display mesogenic properties, as found for some purely organic perylene diimide compounds.¹⁵ The compounds have fairly low melting points, but are not mesomorphic.

The phosphine complexes 4a,b, 5a, 7a and 8a were easily prepared in good yield, as yellow solids, by oxidative addition of R-PerC₆F₄X (R = H, C₆H₁₃; X = Br, I) to an appropriate Pd(0)or Pt(0) precursor. Metathesis of 4a with one molar equivalent of KSCN leads to 6a, for which the value 2081 cm⁻¹ for ν (C=N) suggests N-coordination of the thiocyanato ligand.¹⁶ This was confirmed by X-ray diffraction methods (see later). These palladium derivatives are yellow solids, and are more soluble than the starting organic precursors. The ¹H NMR spectra of the complexes show the expected resonances as above. The ${}^{31}P{}^{1}H$ NMR spectra of the Pd complexes 4-6 show a singlet, consistent with a trans arrangement of the two phosphines. The ¹⁹F NMR spectra show two complicated multiplets, in the range -116 and -119 ppm for Fortho and ca. -142 ppm for F_{meta} , by coupling to the two ³¹P atoms (AA'MM' X_2 system). The ³¹P{¹H} NMR spectra of the platinum complexes are also consistent with a trans arrangement of the two phosphines and show a singlet with ¹⁹⁵Pt satellites, at ca. 13.8 ppm for 7a and 33.0 ppm for 8a. The ${}^{1}J_{PtP}$ values (2440 Hz) are in the range for a trans-P-Pt-P configuration.^{5,17} The ¹⁹F NMR spectra show two multiplet signals (as for Pd) further complicated with ¹⁹⁵Pt satellites, at ca. -119.2 ppm $(J_{Pt-F} = 446 \text{ Hz})$ for F_{ortho} and $-142.7 \text{ ppm} (J_{Pt-F} = 120 \text{ Hz})$ for Fmeta.

X-ray crystal structures

The structures of **1**, **2a**, and **6a** were determined by singlecrystal X-ray diffraction methods, and are shown in Fig. 1. Selected bond lengths and angles are given in Tables 1 and 2.



Fig. 1 ORTEP of the crystal structures of 1, 2a, and 6a. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity).

 Table 1
 Selected interatomic distances (Å) and angles (°) for 1. Data for the second molecule are given in the ESI

$\begin{array}{ccccc} Co(1)-Co(2) & 2.459(2) & C(1)-C(21) & 1.473(10) \\ Co(1)-C(22) & 1.974(8) & C(31)-O(1) & 1.139(9) \\ Co(1)-C(21) & 2.001(8) & C(32)-O(2) & 1.134(10) \\ Co(2)-C(21) & 1.971(8) & C(33)-O(3) & 1.133(10) \\ Co(2)-C(22) & 1.951(8) & C(34)-O(4) & 1.146(9) \\ C(21)-C(22) & 1.337(10) & C(35)-O(5) & 1.141(10) \\ C(22)-C(23) & 1.520(10) & C(36)-O(6) & 1.149(10) \\ \end{array}$				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} \text{Co}(1)-\text{Co}(2) \\ \text{Co}(1)-\text{C}(22) \\ \text{Co}(1)-\text{C}(21) \\ \text{Co}(2)-\text{C}(21) \\ \text{Co}(2)-\text{C}(22) \\ \text{C}(21)-\text{C}(22) \\ \text{C}(21)-\text{C}(22) \\ \text{C}(22)-\text{C}(23) \end{array}$	2.459(2) 1.974(8) 2.001(8) 1.971(8) 1.951(8) 1.337(10) 1.520(10)	$\begin{array}{c} C(1)-C(21)\\ C(31)-O(1)\\ C(32)-O(2)\\ C(33)-O(3)\\ C(33)-O(3)\\ C(34)-O(4)\\ C(35)-O(5)\\ C(35)-O(6) \end{array}$	$\begin{array}{c} 1.473(10)\\ 1.139(9)\\ 1.134(10)\\ 1.133(10)\\ 1.146(9)\\ 1.141(10)\\ 1.149(10)\end{array}$
	C(22)-C(23) C(22)-Co(1)-Co(2) C(21)-Co(1)-Co(2) C(22)-Co(2)-Co(1) C(21)-Co(2)-Co(1)	50.8(2) 51.2(2) 51.6(2) 52.3(2)	C(1)-C(21)-Co(2) C(1)-C(21)-Co(1) C(21)-C(22)-Co(2) C(21)-C(22)-Co(1)	1.149(10) $131.8(5)$ $136.1(5)$ $70.9(5)$ $71.5(5)$

Data collection and refinement parameters are given in the Experimental section.

Complex 1 crystallizes in the triclinic space group $P\bar{1}$, with two molecules per asymmetric being chemically equivalent,

Table 2 Selected interatomic distances (Å) and angles (°) for 2a and for 6a

2a		6a	
Au(1)-C(1)	1.999(12)	Pd(1)-C(1)	2.000(4)
Au(1)-C(27)	1.964(13)	Pd(1) - P(1)	2.3617(13)
C(27) - N(1)	1.115(15)	Pd(1)-P(2)	2.3239(13)
N(1) - C(28)	1.502(18)	Pd(1) - N(1)	2.131(6)
		N(1) - C(27)	0.937(6)
C(27)-Au(1)-C(1)	178.1(5)	C(27) - S(1)	1.724(5)
N(1) - C(27) - Au(1)	179.4(14)	C(1) - Pd(1) - N	176.15(17)
C(27)-N(1)-C(28)	179.4(17)	C(1) - Pd(1) - P(1)	90.78(12)
C(2) - C(1) - C(6)	112.7(11)	N-Pd(1)-P(1)	91.57(11)
		C(1) - Pd(1) - P(2)	91.12(12)
		N-Pd(1)-P(2)	86.82(11)
		P(1) - Pd(1) - P(2)	174.44(4)
		N(1)-C(27)-S(1)	174.1(6)
		C(27) - N(1) - Pd(1)	167.8(5)
		C(2) - C(1) - C(6)	113.2(4)



Fig. 2 Molecular arrangement into dimers in the crystal structure of 2a.

and only one of them is represented in Fig. 1. These differ mostly in the arrangement of the butyl chain with respect to the perylene. The structure contains a tetrahedral Co_2C_2 unit with the C(21)–C(22) bond essentially perpendicular to the Co(1)–Co(2) bond. In addition, the alkyne unit C(21)–C(22) is substituted with a perylenyl group at C(21) and a butyl group at C(22), whereas the two cobalt atoms Co(1) and Co(2) are each bound to three terminal carbonyls. The Co(1)–Co(2) (2.459(2) Å) and C(21)–C(22) (1.337(10) Å) distances as well as the C(1)–C(21)–C(22) (144.6(7)°) and C(21)–C(22)–C(23) (140.6(7)°) angles are similar to those found for other tetrahedral Co₂C₂ systems.^{10,18}

The perylenyl fragments in complexes **2a** or **6a** are essentially planar (the dihedral angles between the two "naphthalene" moieties forming the perylene are 2.69° (**2a**) and 3.69° (**6a**)), and make dihedral angles to the tetrafluorophenyl plane of 57.49° (**2a**) and 77.75° (**6a**). The C–C–C angles at the ipso carbon of the C₆F₄ group in both complexes are less than 120° (112.7(11)° and 113.2(4)° for **2a** and **6a**, respectively), because of electronic effects of the electropositive metal and electronegative fluorine substituents at the *ortho* positions.¹⁹

The gold coordination in **2a** is almost perfectly linear, with C(1)–Au–C(27) bond angles of 178.1° and 179.4° for N(1)–C(27)–Au. The bond lengths Au–C(1) (tetrafluorophenyl) (1.999(12) Å) and Au–C(27) (isocyanide) are comparable to related aryl-gold and isocyanide-gold complexes.^{20,21} The molecular packing features the association of two monomers (Fig. 2) arranged almost antiparallel, with an Au—Au distance

of 3.114 Å, which is within the range proposed for aurophilic interactions. $^{\rm 22}$

In complex **6a**, the Pd(II) center shows a slightly distorted square planar geometry. Confirming the spectroscopic studies, the PEt₃ ligands are in *trans* configuration, with a P(1)–Pd–P(2) angle of 174.4°. As expected, the thiocyanate is N-bonded, with C(27)–N(1)–Pd and N(1)–C(27)–S(1) bond angles only slightly deviated from linearity (167.8(5)° and 174.1(6)°, respectively). The Pd–N distance (2.131(6) Å) is longer than those found in most thiocyanato-palladium(II) complexes, reflecting the high *trans*-influence of the tetrafluorophenyl group.²³

Finally, the potential π - π stacking aggregation of molecules, often found for organic compounds with extended aromatic cores, is not observed for any of the complexes, which helps for the higher solubility observed.

Photophysical studies

(a) UV-Vis absorption spectra. The UV-Vis absorption and emission spectra of dilute solutions of the metal complexes in chloroform ($c \sim 10^{-5}$ M) are summarized in Table 3. On the other hand, the absorption spectra of perylene, Per-C=C-C₄H₉, PerC₆F₄H, and C₆-PerC₆F₄H are compared with those of complexes **1-8** in Fig. 3, to see the influence of the chain or the C₆F₄ML_n group on the photophysical properties as compared to perylene.

The profiles of the UV-Vis absorptions of perylene, Per-C==C-C₄H₉, PerC₆F₄H, C₆PerC₆F₄H, and their related complexes **1–8** are closely related, and are dominated by the π - π * transition of the perylene moiety. The absorption spectra consist of two strong transitions, a broad very intense one in the UV, at 240–315 nm, and a second one in the visible, at 350–475 nm, with a vibronic structure; for **1** the coordination to Co₂(CO)₆ results in loss of the fine structure and significant broadening of the spectrum, extending to approximately 700 nm. The vibronic structure, with a vibrational spacing of ~1300 cm⁻¹, is related to the ν (C==C) frequency of the polyaromatic system.

The perturbation on the perylene spectrum observed in the visible for the C_6F_4H group is quite similar (444 nm for C_6F_4H versus 439 nm for perylene, that is $\sim 260 \text{ cm}^{-1}$) and only moderately different to that produced by the $(C_6F_4)ML_n$ fragments (further 0-230 cm⁻¹). This is in contrast with our previous observations of larger effects for $Pt(PEt_3)_2X$ groups (X = NCS, CN, NO₃, CN^tBu, PyMe) σ -bonded directly to the perylene core.⁵ Moreover, the absorptions for **1–8** show also a very small solvent dependence. For example, when the solvent is changed from toluene to acetonitrile, the lowest energy bands of 8 are red-shifted only by less than 300 cm^{-1} (see Fig. S1 in ESI⁺). This behaviour suggests that these bands are most probably intraligand π - π^* transitions rather than charge transfers. It also supports the fact that the electronic connection of the perylene and the metal fragments through the C₆F₄ link is very weak, which is due to the large dihedral angle between the perylene and the C₆F₄ rings observed in the X-ray structures.

Table 3 UV-Vis absorption, excitation and emission data for Per-C=C-C₄H₉, PerC₆F₄H, C₆PerC₆F₄H and their complexes **1–8**, in CHCl₃ at 298 K, and half-wave redox potentials in CH₂Cl₂

Compound	$\lambda(nm) (10^{-3} \epsilon)/dm^3 mol^{-1} cm^{-1}$	$\lambda_{\rm ex}/{\rm nm}$	$\lambda_{\rm em}/{\rm nm}$	Φ^{a}	τ^b/ns	$E_{1 \text{ox}}$
PerC ₆ F ₄ H	255 (39.6), 398 (12.5), 417 (27.8), 444 (33.5)	418, 443	460, 485	0.96	4.34 (1.027)	1.12
C ₆ PerC ₆ F ₄ H	256 (46.9.2), 396 (12.3), 421 (30.3), 446 (37.0)	423, 448	466	0.96	4.30 (1.077)	1.03
Per-C≡C-Bu	259 (48.1), 408 (15.3), 431 (31.4), 459 (38.9)	431, 458	465, 496	0.80	4.32 (1.120)	1.08^{d}
1	257 (32.8), 457 (17.3), 477sh (13.7), 596sh (2.4)	432, 455	465, 494	0.37	3.93 (1.030)	1.08^{d}
2a	259 (77), 398 (13.3), 419 (29.4), 445 (37)	418, 443	460, 487	0.85	4.06 (1.027)	1.08
3a	257 (80), 274 (72.7), 398 (15.6), 420 (33.6), 445 (42)	418, 443	461, 488	0.95	3.35 (1.050)	1.08
3b	257 (56.4), 276 (35.1), 402 (18.1), 425 (35.5), 452 (44.2)	428, 452	469, 496	0.93	3.44 (1.016)	1.02
4a	249 (74.6), 399 (18.3), 421 (37.2), 447 (45.6)	420, 446	461, 489	0.19	0.25 [49.3], 2.18 [50.7] (1.034) ^c	1.06
4b	241 (67.1), 257 (64.2), 402 (16.5), 428 (35.6), 454 (43.8)	427, 454	469, 497	0.16	0.41 [48.4], 2.42 [51.6] (1.044) ^c	1.03
5a	256 (66.3), 398 (14.7), 420 (30.6), 445 (37.9)	419, 444	460, 488	0.80	3.48 (1.017)	1.08
6a	257 (50.9), 399 (15.0), 421 (25.0), 445 (30.6)	420, 446	461, 488	0.71	2.09 (1.024)	1.07
7a	256 (56.2), 398 (19.5), 420 (31.0), 445 (38.3)	419, 444	461, 487	0.83	3.59 (1.011)	1.08
8a	256 (48.7), 398 (15.5), 420 (32.8), 445 (40.8)	419, 445	461, 488	0.86	3.63 (1.020)	1.10

^{*a*} Quantum yield. ^{*b*} Fluorescence lifetimes in dichloromethane; numbers in parentheses indicate the χ^2 values of the fits obtained by deconvolution. ^{*c*} Decays were bi-exponential; numbers in brackets indicate the relative amplitude of components. ^{*d*} Irreversible oxidation peak.

Molecular orbital calculations

DFT calculations were performed on representative PerC₆F₄Y compounds in order to better understand their absorption spectra. The selected molecular species were PerC₆F₄H, $PerC_6F_5$, $(PerC_6F_4)Au(CNMe),$ $(PerC_6F_4)PdBr(PMe_3)_2$ and (PerC₆F₄)PtBr(PMe₃)₂. Their optimized theoretical structures are available in the ESI.[†] The main calculated geometric parameters match the experimental observations. For example, the naphthalene moieties are practically coplanar having only small dihedral angles between the naphthalene halves: ca. 1° for the organic molecules, 2° for Au, and 3° in the Pd and Pt derivatives. The tetrafluorophenyl and perylene planes are staggered, with dihedral angles of 60° in the organic molecules and 62° in their metal complexes. The dihedral angles of perylene with the square-planar coordination planes of Pd and Pt come close to coplanarity (8° for Pd and 7° for Pt). Finally, C-H…F-C contacts are present in all the calculated structures with 2.6-2.86 Å distances, within the range of experimental data.²⁴

The absorption spectra were calculated by TD-DFT, in the gas phase and in CHCl₃. In the organic compound PerC₆F₄H (Table 4) two bands at 442 and 256 nm are predicted, as observed. The first peak is the most intense one ($f \approx 0.49$), and it corresponds to a HOMO \rightarrow LUMO transition. These orbitals can be described as the antisymmetric and symmetric combinations of π^* orbitals of two naphthalene moieties of the perylene, respectively. Since these orbitals are essentially centered in the perylene fragment without any significant contribution of the fluoroaryl ring, this energy gap (0.11 au \approx 3 eV) is almost the same for the metal complexes. A second band, at \sim 256 nm, has lower intensity than the former, and is assigned to a combination of several transitions between π orbitals of the perylene. The major contributions are transitions between the lower occupied MO and the LUMO and between the HOMO and a higher empty MO ($\pi^*(\text{Per})$ in Fig. 4). In the gas

phase, the first contribution (internal MO \rightarrow LUMO) is more important than the second, but in solution the opposite holds. For simplicity only, the HOMO $\rightarrow \pi^*(\text{Per})$ transition is depicted in Fig. 4.

The spectra of the complexes containing the $(PerC_6F_4)Au$ -(CNMe), (PerC₆F₄)PdBr(PMe₃)₂ and (PerC₆F₄)PtBr(PMe₃)₂ fragments were also calculated. The transitions and orbitals involved are shown in Fig. 4 for (PerC₆F₄)AuCNMe, and are given in the ESI^{\dagger} for (PerC₆F₄)PdBr(PMe₃)₂ and (PerC₆F₄) $PtBr(PMe_3)_2$. In the three complexes the lower energy bands correspond to the HOMO \rightarrow LUMO transition and are calculated to appear at 448 nm (Au) and 443 nm (Pd and Pt) in the gas phase, and 457 nm (Au), 456 nm (Pd) and 457 nm (Pt) in CHCl₃. This is in satisfactory concordance with the experimental values of 445 nm (2a), 445 nm (5a), and 445 nm (7a). Since the involved orbitals are centered in the perylene fragment, the wavelength values associated with these absorptions are very similar to that found for PerC₆F₄H. The calculations predict an increased intensity (ca. 20%), compared to the free ligand, for the bands in the complexes. This is also in agreement with the experiment (experimental values: ε = 33 for the free ligand *versus* ε = 37 for complexes).

The calculations for the Au complex predict, in addition, absorptions in the ranges 293–288 and 254–231 nm. According to the analysis of the orbitals, the peak at 293 nm is assigned to a transition from π to π^* orbitals of the perylene (Fig. 4) and is related to those observed for PerC₆F₄H at *ca.* 256 nm. The shift observed is due to the electron withdrawing effect of the C₆F₄ group. However, when a solvent effect is introduced, this contribution decreases in the low-intensity band at 291 nm, increasing the intensity in a band at 260 nm (which is centered in a transfer from the perylene π system to the tetrafluorophenyl ring and the isocyanide ligand in the gas phase). The peak at 288 nm is clearly assigned to a charge transfer from the tetrafluorophenyl ring to the isocyanide ligand, in concordance with our calculation for the complex (C₆F₅)Au(CNMe)



Fig. 3 Absorption spectra, recorded in $CHCl_3$ solution ($\sim 10^{-5}$ M) at room temperature, for perylene, $Per-C \equiv C-C_4H_9$, $PerC_6F_4H$, $C_6PerC_6F_4H$ and their complexes **1–8**.

(287 nm). According to calculations this LLCT is very sensitive to solvent effect in both complexes and is calculated to be blue shifted to 266 and 262 nm, respectively, with increasing intensity. Analogously, the peak at 254 nm is assigned to a charge transfer from the perylene π system to the isocyanide ligand, and calculations predict a red shift in CHCl₃ to 239 nm. Consequently, these two absorptions should converge in the similar region with larger intensity in solution, and can be observed in **3a–b**, although only a shoulder can be appreciated in **2a**. Finally, interligand transfer bands from the perylene π system to the isocyanide ligand are calculated at 254 nm (239 nm in solution), and interligand transfer bands from the tetrafluorophenyl ring to the perylene fragment are predicted to be below 240 nm.

For $(PerC_6F_4)PdBr(PMe_3)_2$ and $(PerC_6F_4)PtBr(PMe_3)_2$ complexes, the two calculated bands related with the perylene

	PerC ₆ F ₄ H		(PerC ₆ F ₄)Au(CNMe)		
Assignment	Gas phase	$CHCl_3$	Gas phase	CHCl ₃	
Perylene: HOMO → LUMO	442 (0.49)	455 (0.62)	448 (0.59)	457 (0.72)	
Perylene: $\pi \to \pi^*$	257(0.13) 255(0.15)	259 (0.36) 257 (0.09)	293 (0.11)	291 (0.03) 260 (0.33)	
LLCT: $C_6F_4 \rightarrow CNMe$ LLCT: Perylene $\rightarrow CNR$ LLCT: Perylene $\rightarrow C_6F_4$ LLCT: $C_6F_4 \rightarrow Perylene$			$\begin{array}{c} 288 \ (0.18) \\ 254 \ (0.08) \\ 252 \ (0.08) \\ 231 \ (0.22) \end{array}$	266 (0.46) 239 (0.06) 255 (0.06) 227 (0.18)	

fragment (443 and 256 nm in the gas phase and 456 and 259 in $CHCl_3$, respectively) do not change significantly. The electronic structure and orbital analysis of both complexes are discussed in the ESI.[†]

It is worth noting that the TD-DFT calculations show clearly that the frontier orbitals of the C_6F_4 group do not interact with the frontier orbitals of the perylene ligands. Consequently the M orbitals cannot interact, even indirectly, with the perylene orbitals through the C_6F_4 group and all the transitions occur between singlet states.²⁵ This is confirmed by the photophysical properties discussed below.

(b) Luminescence spectra. The luminescence spectra of PerC₆F₄, PerC≡C-Bu, C₆PerC₆F₄ and their related complexes 1-8 at room temperature in chloroform are listed in Table 3. All complexes exhibit strong luminescence in solution and display emission bands with a well-defined vibronic structure in the range 450-550 nm (see Fig. 4), which can be correlated to those for perylene at about 425-525 nm. The similarity of the overall luminescence spectra of these complexes with the perylene strongly suggests a ligand-dominated emissive state that can be assigned as intraligand π - π * disturbed by the substituents. On the basis of the similar Stokes shifts between absorption and emission (less than 1000 cm^{-1} in all cases) the luminescence observed can be assigned to π - π * fluorescence,²⁶ which was supported by the fact that the emission properties remaining unchanged in the presence of air would be consistent with this assignment.²⁷ This was further confirmed with the measurement of their emission lifetimes, in the range 0.2-4.4 ns (Table 3). The emission lifetimes obtained for the complexes are similar. Usually, these ligands and complexes show mono-exponential decay with lower lifetimes for the metal derivatives. In contrast, 4a,b show bi-exponential decay with two approximately equal components, one of about 0.3 ns and another substantially longer of about 2.2 ns.

As shown in Fig. 5, the emission band in compound 1 relative to PerC=C-Bu (Fig. 5 above) did not show any shift, suggesting that the emission is fully perylene based, without significant MLCT contribution by coordination to $Co_2(CO)_6$. For the tetrafluorophenylperylene derivatives, Fig. 5 shows normalized emission spectra in chloroform solutions of 2–8.

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Fig. 4 Schematic representation of the main electronic transitions expected in the absorption spectra for PerC₆F₄H and (PerC₆F₄)AuCNMe.

Bands at $\lambda_{\text{max}} = 461$ or 469 nm, for the tetrafluorophenyperylenyl complexes without or with an alkyl chain attached to perylene, respectively, are observed, with a vibronic structure similar to that observed for the perylene parent but less well defined (Fig. 5 below). Comparison of the emission spectra of the metal complexes 2–8 with those found for the tetrafluorophenyl ligands reveals that the ML_n group does not exert significant influence on the long-wavelength emission maxima.

The effect of different solvents (acetonitrile, chloroform and toluene) on the emission spectra of **8a** was studied at room temperature (Fig. S2 in the ESI⁺). The nearly identical emission spectra (<200 cm⁻¹) indicate that the fluorescence of the per-fluorophenyl derivatives is hardly sensitive to the polarity of the solvents.

Quantum yields

Although the presence of heavy atoms is usually detrimental for quantum yields, there are a few literature reports of metal complexes showing high fluorescence values. This is the case of perylene substituted organotrialkynyltin compounds where an alkyl chain connects the perylene core with a trialkynylstannyl group, thus insulating the fluorophore from the metal;²⁸ or the case of perylene bisimide metal complexes with a 4-pyridine unit connecting the bisimide to a Pd(π) or Pt(π) diphosphine complex;²⁹ similar results have been reported for two palladium complexes of perylene diimides attached to the bay region,²⁵ which also show strong fluorescence ($\Phi_{\rm fl} = 0.65$ and 0.22), or for perylenyl complexes containing a Pt(PEt₃)₂X group (70–80% of the fluorescence of the mother organic molecule).⁵ In contrast, for Pt(π) complexes ligated *via* an acetylide bridge in the bay region to perylenediimide moieties, the fluorescence is totally quenched;³⁰ the intense fluorescence of diazadibenzoperylene ($\Phi_{\rm fl} = 0.80$) is also strongly quenched upon metal coordination.³¹

For the compounds reported here, the emission quantum yields, $\Phi_{\rm fl}$, for PerC₆F₄H, C₆PerC₆F₄H, and complexes **1–8**, measured in dichloromethane at room temperature were determined using perylene in ethanol as standard ($\Phi_{\rm fl}$ =



Fig. 5 Emission spectra recorded in CHCl₃ solution ($\sim 10^{-5}$ M) at room temperature, for Per-C=C-C₄H₉, PerC₆F₄H, C₆PerC₆F₄H and their complexes **1–8**.

0.92),³² with an excitation wavelength of 407 nm. The complexes are highly fluorescent, with quantum yields in the range 0.16–0.95 (Table 3). A reduction in emission intensity for the dicobalt complex 1 ($\Phi_{\rm fl} = 0.37$) is observed compared to the uncomplexed perylenyl precursor PerC=C-Bu ($\Phi_{\rm fl} = 0.80$), but this reduction is less than the decrease found in related pyrenyl complexes (up to 95% decrease).⁹ Complexes 2–8 exhibit high $\Phi_{\rm fl}$ values, all higher than 0.7 except for the palladium complexes 4a and 4b that exhibit unexpectedly low fluorescence quantum yield (Table 3).

A strong to good conservation of luminescence in our complexes can be attributed to the very good insulation of the frontier empty π^* orbitals of the perylene fragment from the heavy metal filled orbitals through the C_6F_4 connector group, which makes a large dihedral angle to the perylene plane leading to an efficient electronic decoupling of the metal fragment from the HOMO and LUMO of the perylene chromophore. As the presence of different metal centres (Au, Pd, Pt) in these tetrafluorophenylperylenyl complexes has little effect on the emission maxima and intensity relative to perylene, the introduction of different substituents attached to the various auxiliary metal centers does not disturb the photophysical properties of perylene. This makes the linking system an interesting one for application, for a number of reasons: (i) it makes strong bonds with late transition metals; (ii) the presence of ancillary ligands, and the link itself, help to increase the solubility of the complexes; (iii) the high conservation of the positions and luminescence of the perylene bands in the complexes can be used to trace the presence of these complexes in different experimental conditions by luminescence studies; (iv) the presence of the C_6F_4 link can be also used for studies by ¹⁹F NMR, avoiding the interference of solvents that occurs in ¹H NMR studies. Metal complexes with luminescent markers are of interest in a number of fields, for instance in biological studies.³³

The electrochemical properties of the compounds have been measured in CH₂Cl₂ by cyclic voltammetry, in the range +1.6 to -1.8 V, and are listed in Table 3. For the tetrafluorophenyl derivatives 2a-8a only one reversible wave was found within the range studied, at ca. +1.08 V, with a slightly decrease in the potential of 0.04 V, relative to PerC₆F₄H, (+1.12 V). The latter is very similar to pervlene (+1.06 V).³⁴ The derivatives 3b and 4b (with an hexyl substituent on the perylene core) are slightly easier to oxidize (+1.02 V), due to the electron-donating nature of the alkyl substituent. The oxidation of Per-C=C-Bu and complex 1 displays one irreversible wave during the first cycle. Thus, the trends observed for the redox processes and for the luminescence energies are roughly coincident, as expected, confirming the insulation between the π system of the perylenyl group and the metal fragments connected to it through the C_6F_4 link.

Conclusions

Two tetrafluorophenylperylenes, $PerC_6F_4H$ and $C_6PerC_6F_4H$, and several metallated complexes have been successfully prepared. In most cases, attaching the heavy metal unit to the fluorophore with C_6F_4 as a spacer does not significantly affect the fluorescence properties of the perylene parents. Theoretical calculations of the absorption spectra of the $PerC_6F_4-Y$ compounds (Y = H, F, Au(CNMe), PtBr(PMe_3)_2 and PdBr-(PMe_3)_2) support the fact that these are independent of the substituent because the π systems of the perylene and tetrafluorophenyl fragments are uncoupled, according to the poor coplanarity found in the molecular structure. Since these complexes are highly luminescent and practically keep the optical properties of perylene, they could be used as easily detected markers.

Experimental section

Materials and general methods

All reactions were carried out under dry nitrogen. The solvents were purified according to standard procedures. Literature methods were used to prepare AuCl(tht),³⁵ Pd₂(dba)₃,³⁶ Pt(PEt₃)₄,³⁷ 1,2,3-tris(dodecyloxy)-5-isocyanobenzene,³⁸ 3-(1-hexynyl)perylene,⁸ and 3-bromo-9(10)-hexylperylene.⁸ C, H, N analyses were carried out on a Perkin-Elmer 2400 micro-analyzer. IR spectra (cm⁻¹) were recorded on a Perkin-Elmer FT-1720X spectrometer. ¹H and ³¹P NMR spectra were recorded on a Bruker AC 300 or Bruker 400 MHz spectrophotometer in

CDCl₃, with chemical shifts referred to TMS and 85% H₃PO₄, respectively. UV-vis absorption spectra were obtained on a Shimadzu UV-1603 spectrophotometer, in chloroform solution $(1 \times 10^{-5} \text{ M})$. Luminescence data were recorded on a Perkin-Elmer LS-luminescence spectrometer, in CHCl₃ (1×10^{-5} M). Luminescence quantum yields were obtained at room temperature using the optically dilute method (A < 0.1) in degassed dichloromethane (quantum yields standard was perylene in ethanol, $\Phi_{\rm fl} = 0.92$,³² and using an excitation wavelength of 407 nm in dichloromethane). The emission lifetime measurements were carried out with a Lifespec-red picosecond fluorescence lifetime spectrometer from Edinburgh Instruments. As excitation sources two diode lasers, with 405 and 470 nm nominal wavelengths, were used. The first wavelength (405 nm) has a pulse width of 88.5 picoseconds, and its typical average power is 0.40 mW. The second wavelength (470 nm) has a pulse width of 97.2 picoseconds, and its typical average power is 0.15 mW. The pulse period is 1 µs and the pulse repetition frequency is 10 MHz. The monochromator slit is 2 nm. The instrument response measured at the HWHM (half width at high maximum) was below 350 picoseconds. The technique used is "Time Correlated Single Photon Counting" (TCSPC). Mono-exponential and bi-exponential fluorescence decay models were fitted to each decay. Eqn (1) describes the monoexponential decay model:

$$I(t) = I_0 \exp(-t/\tau) \tag{1}$$

where I_0 is the relative intensity, t is the time and τ is the fluorescence lifetime, both expressed in ns. The bi-exponential decay model is expressed by eqn (2) as

$$I(t) = F_1 \exp(-t/\tau_1) + F_2 \exp(-t/\tau_2)$$
(2)

where F_1 and F_2 are the relative intensities associated with two lifetimes, τ_1 and τ_2 , respectively.

Mono-exponential models are normally used to fit fluorescence decay. Bi-exponential fits may be more appropriate for samples containing non-linear decays. Fitting was done using FAST software from Edinburgh Instruments by a least-squares algorithm using a reconvolution approach. In this method, convolution of eqn (1) or (2) with the instrumental response function (IRF) is done prior to evaluating the goodness of fit with a weighted χ^2 parameter. The bi-exponential decay model represents the data better than a single decay for samples **4a** and **4b** as evidenced by the even distribution of the residuals about zero. An extra parameter to the model, the ratio of F_1 to F_2 , is also given.

Electrochemical measurements

Electrochemical studies employed cyclic voltammetry using a potentiostat EG&G model 273. The three-electrode system was equipped with a platinum (3 mm diameter) working electrode, a saturated calomel reference electrode (SCE), and a Pt wire counter electrode. The electro-chemical potentials were calibrated relative to SCE using ferrocene as an internal standard (Fc/Fc⁺) at +0.46 V νs . SCE).³⁹ Tetra-*n*-butylammonium

hexafluorophosphate (0.1 M) in CH_2Cl_2 was used as a supporting electrolyte and the solutions of the complexes were in the order 10^{-3} M. All scans were done at 100 mV s⁻¹.

Computational details

Unrestricted calculations were carried out using the Gaussian09 package.⁴⁰ The hybrid density function method B3LYP was applied.⁴¹ Effective core potentials (ECP) were used to represent the innermost electrons of the transition atoms (Au, Pt and Pd) and the basis set of valence double-z quality was associated with the pseudopotentials LANL2DZ.⁴² The basis set for the main group elements was 6-31G* (Br, P, C, N, F and H).⁴³ Solvent effects of chloroform were taken into account by PCM calculations,⁴⁴ keeping the geometry optimized for the gas phase (single-point calculations). Excited states and absorption spectra were obtained from the time-depending algorithm implemented in Gaussian09,⁴⁵ using the B3LYP functional (a benchmark for the perylene molecule shows a more accurate wavelength than the PBE one, 445 and 480 nm respectively).

3-(2,3,5,6-Tetrafluorophenyl)perylene (PerC₆ F_4 H). K₂CO₃ (0.460 g, 3.33 mmol), P^tBu₂Me-HBF₄ (75 mg, 0.30 mmol), Pd-(OAc)₂ (34 mg, 0.15 mmol) and 3-bromoperylene (1.0 g, 3.02 mmol) were added in a Schlenk tube under N2 atmosphere. 1,2,4,5 Tetrafluorobenzene (1.01 mL, 9.05 mmol) and DMA (20 mL) were then added via a syringe and the reaction was heated to 120 °C for 15 h. The solvent was then evaporated and the black residue purified by loading the crude reaction mixture directly onto a silica gel packed flash chromatography column using hexane-ethyl acetate (7:1) as an eluent ($R_{\rm f}$ = 0.4). Yield 0.670 g (56%). The product contains ca. 3% of perylene (by ¹H NMR integration). ¹H NMR (300 MHz, CDCl₃): δ 8.3-8.23 (m, 4H), 7.65-7.28 (m, 2H), 7.56-7.46 (m, 4H), 7.38–7.35 (m, 1H), 7.21 (m, 1H). ¹⁹F NMR (CDCl₃): δ –139.1 $(m, 2F_{ortho}), -140.3 (m, 2F_{meta})$. MS (m/z): 400.

3-Tetrafluorophenyl-9(10)hexylperylene ($C_6PerC_6F_4H$). 3-Tetrafluorophenyl-9(10)hexylperylene was prepared similarly to PerC₆F₄ using 3-bromo-9(10)-hexylperylene. Yield: 0.305 g (35%). R_f (silicagel, hexane–ethyl acetate 7 : 1) = 0.5. Anal. calcd for $C_{32}H_{24}F_4$ (484.54): C, 79.32; H, 4.99. Found: C, 78.92; H, 4.76. ¹H NMR (300 MHz, CDCl₃): δ 8.28–8.14 (m, 4H), 7.65–7.11 (m, 1H), 7.56–7.46 (m, 4H), 7.37–7.34 (m, 1H), 7.25–7.16 (m, 1H). ¹⁹F NMR (CDCl₃): δ –139.2 (m, 2 F_{ortho}), –140.3 (m, 2 F_{meta}). MS (m/z): 484.

PerC₆F₄Br. To a solution of $PerC_6F_4$ (0.161 g, 0.402 mmol) in dry THF (25 mL) was added dropwise a solution of *n*-BuLi in hexane (0.27 mL, 1.6 M, 0.442 mmol) at -78 °C, under N₂ atmosphere. After the solution was stirred at -60 °C for 2 h, Br₂ (0.1 mL, 12 mmol) was added at -78 °C and the reaction mixture was slowly brought to room temperature (3 h). Then, a saturated aqueous solution of Na₂S₂O₃ (7 mL) was added and the mixture stirred for 0.5 h. The solvent was removed in vacuum and the resulting orange residue was redissolved in dichloromethane (20 mL), and the solution dried with anhydrous MgSO₄. Then, the solution was filtered through a Kieselguhr filter, and the solvent was evaporated to obtain an orange solid. The solid was washed with diethyl ether (2 × 5 mL) and dried under vacuum. Yield: 0.180 g, 93% (contains *ca.* 3% of perylene (by ¹H NMR integration)). ¹H NMR (300 MHz, CDCl₃): δ 8.3–8.24 (m, 4H), 7.65–7.28 (m, 2H), 7.56–7.46 (m, 4H), 7.37–7.34 (m, 1H). ¹⁹F NMR (CDCl₃): δ –133.4 (m, 2F_{ortho}), –138.4 (m, 2F_{meta}). MS (*m*/*z*): 478.

PerC₆F₄I and C₆PerC₆F₄I. The method was the same as above but used I₂ instead of Br₂. 3-(2,3,5,6-Tetrafluoro-4-iodophenyl)perylene, yield: 0.780 g (94%) (the product contains *ca.* 5% of perylene (by ¹H NMR integration)). ¹H NMR (300 MHz, CDCl₃): δ 8.30–8.24 (m, 4H), 7.65–7.28 (m, 2H), 7.56–7.46 (m, 4H), 7.35 (m, 1H). ¹⁹F NMR (CDCl₃): δ –120.61 (m, 2F_{ortho}), -137.9 (m, 2F_{meta}). MS (*m*/*z*): 526.

3-(2,3,5,6-Tetrafluoro-4-iodophenyl)-9(10)hexylperylene, yield: 0.300 g (70%). ¹H NMR (300 MHz, CDCl₃): δ 8.30–8.24 (m, 4H), 7.65–7.28 (m, 2H), 7.56–7.46 (m, 4H), 7.36 (m, 1H). ¹⁹F NMR (CDCl₃): δ –122.1 (m, 2F_{ortho}), –139.2 (m, 2F_{meta}).

[Co₂(CO)₆(μ−η²-C₄H₉C=C-Per)] (1). To a solution of 3-(1-hexynyl)perylene (60 mg, 0.181 mmol) in 20 mL of dried dichloromethane (20 mL) was added Co₂(CO)₈ (64 mg, 0.187 mmol). The resulting solution was stirred for 3 h to yield a dark green solution. The solution was filtered through a Kieselguhr filter, concentrated to *ca.* 10 mL and the dark green solid 1 was precipitated by the addition of 30 mL of methanol. Yield: 55 mg (50%). Anal. calcd for C₃₂H₂₀Co₂O₆: C, 62.16; H, 3.26. Found: C, 62.05; H, 3.10. ¹H NMR (400 MHz, CDCl₃): δ 8.27–8.18 (m, 4H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.60 (m, 1H), 7.50 (m, 2H), 3.33 (t, *J* = 8.1 Hz, 2H, *CH*₂), 1.75–1.71 (m, 2H, *CH*₂), 1.55–1.50 (m, 2H, *CH*₂), 0.97 (t, *J* = 7.1 Hz, *CH*₃).

 $[Au(PerC_6F_4)(CN^tBu)]$ (2a). To a solution of $PerC_6F_4$ (63 mg, 0.157 mmol) of dried THF (15 mL) was added a solution of LiBu in hexane (0.108 mL, 1.6 M, 0.173 mmol) at -78 °C, under nitrogen. After the solution was stirred for 1 h at -60 °C, solid [ClAu(tht)] (50 mg, 0.157 mmol) was added at -78 °C and the reaction mixture was slowly brought to room temperature (2 h). Then, a few drops of water were added and after CN^tBu (18 µL, 0.16 mmol) and the solution was stirred for 0.5 h. The solvent was then evaporated and the residue was redissolved in CH₂Cl₂, and the solution dried with magnesium sulfate. The solution was filtered through a silicagel filter, and the solvent was then removed in vacuum. The solid was recrystallized from CH₂Cl₂/diethyl ether affording a yellow precipitate 2a, which was vacuum-dried. Yield: 67 mg (67%). Anal. calcd for C31H20AuF4N: C, 54.80; H, 2.97; N, 2.06. Found: C, 54.62; H, 3.06; N, 2.13. ¹H NMR (300 MHz, CDCl₃): δ 8.25 (m, 4H), 7.73 (d, J = 8.31 Hz, J = 3.51 Hz, 2H), 7.55-7.44 (m, 5H), 1.65 (s, 9H, $CN^{t}Bu$). ¹⁹F NMR (CDCl₃): δ –117.8 (m, 2F_{ortho}), $-141.8 \text{ (m, 2F}_{meta}$). IR (KBr, cm⁻¹): 2226 ν (C \equiv N).

[AuRCN(C₆H₂)-3,4,5-(OC₁₂H₂₅)₃] (R = PerC₆F₄ (3a), R = C₆-PerC₆F₄ (3b)). The method was the same as above but used 1,2,3-tris(dodecyloxy)-5-isocyanobenzene instead of CN^tBu and the product was chromatographed on deactivated alumina with CH₂Cl₂-hexane (1:1) as the eluent. **3a**: Yield 70 mg, (40%). Anal. calcd for C₆₉H₈₈AuF₄O₃N: C, 66.17; H, 7.08; N, 1.12. Found: C, 66.20; H, 7.02; N, 1.18. ¹H NMR (300 MHz, CDCl₃): δ 8.25 (m, 4H), 7.72 (m, 2H), 7.40–7.60 (m, 5H), 6.74 (s, 2H, CNC₆H₂), 4.0 (m, 6H, OCH₂)₃, 1.90–1.65 (m, 6H, OCH₂-CH₂), 1.54–1.15 (m, 54H, C₉H₁₈–CH₃)₃, 0.90 (t, 9H, CH₃). ¹⁹F NMR (CDCl₃): δ –117.6 (m, 2F_{ortho}), –141.6 (m, 2F_{meta}). IR (KBr, cm⁻¹): 2213 ν (C=N). 3b: Yield, 110 mg (65%). Anal. calcd for C₇₅H₁₀₀AuO₃NF₄: C, 67.40; H, 7.54; N, 1.05. Found: C, 67.15; H, 7.40; N, 1.10. ¹H NMR (300 MHz, CDCl₃): δ 8.32–8.12 (m, 4H), 7.91 (d, J = 8.3 Hz, 1H), 7.59–7.42 (m, 4H), 7.37 (d, J = 7.5, 1H), 6.75 (s, 2H, CNC₆H₂) 4.0 (m, 6H, OCH₂), 3.03 (t, J = 7.5 Hz, 2H, Per–CH₂), 1.90–1.65 (m, 6H, OCH₂-CH₂), 1.55–1.17 (m, 62H, (C₉H₁₈–CH₃)₃, and C₄H₈–CH₃), 0.95 (m, 12H, CH₃). ¹⁹F NMR (CDCl₃): δ –117.5 (m, 2F_{ortho}), –141.6 (m, 2F_{meta}). IR (KBr, cm⁻¹): 2213 ν (C=N).

trans- $[PdR(PPh_3)_2I]$ (R = $PerC_6F_4$ (4a); R = $C_6-PerC_6F_4$ (4b)). To a solution of Pd₂dba₃ (0.140 g, 0.142 mmol) and PPh₃ (0.150 g, 0.57 mmol) in toluene (12 mL) under N₂ atmosphere was added PerC₆F₄I or C₆PerC₆F₄I (0.285 mmol) and the mixture was stirred for 2 h at 50 °C. Then, the solvent was removed in vacuum and the residue was chromatographed on deactivated alumina with CH_2Cl_2 -hexane (1:1) as the eluent. 4a: Yield: 56%. R_f (CH₂Cl₂-hexano (1:1)): 0.62. Anal. calcd for C₆₂H₄₁F₄IP₂Pd C, 64.35; H, 3.57. Found: C, 64.22; H, 3.79. ¹H NMR (300 MHz, CDCl₃): δ 8.20 (m, 4H), 7.88–7.60 (m, 14H), 7.60–7.30 (m, 21H), 7.16 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H). ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 22.6. ${}^{19}F$ NMR (CDCl₃): δ -118.9 (m, 2Fortho), -141.9 (m, 2Fmeta). 4b: Yield: 0.140 g (56%). Rf $(CH_2Cl_2-hexane (1:1))$: 0.5. Anal. calcd for $C_{68}H_{53}F_4IP_2Pd$: C, 65.79; H, 4.30. Found: C, 65.50; H, 4.05. ¹H NMR (300 MHz, $CDCl_3$: δ 8.25–8.12 (m, 4H), 7.91 (d, J = 8.0 Hz, 1H), 7.82–7.65 (m, 12H), 7.55 (m, 1H) 7.50–7.30 (m, 20H), 7.13 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 3.03 (t, J = 7.5 Hz, 2H, Per-CH₂), 1.78 (m, 2H, Per-CH₂-CH₂-C₄H₉), 1.48 (m, 2H, Per-C₂H₄- $C_{3}H_{6}-CH_{3}$, 1.37 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 22.6. ¹⁹F NMR (CDCl₃): δ –119.1 (m, 2F_{ortho}), -141.9 (m, 2F_{meta}).

trans-[PdR(PEt₃)₂I] (R = PerC₆F₄, (5a); R = C₆-PerC₆F₄ (5b)). The method was the same as for $4a_{,b}$ with $Pd_{2}dba_{3}$ (0.061 g, 0.058 mmol), PEt3 (0.06 mL, 0.33 mmol) and PerC₆F₄I or C₆PerC₆F₄I (0.11 mmol). Yield: 40 mg (42%). Rf $(CH_2Cl_2$ -hexane (1:2): 0.62. Anal. calcd for $C_{38}H_{41}F_4IP_2Pd$: C, 52.52; H, 4.76. Found: C, 52.22; H, 4.58. ¹H NMR (300 MHz, CDCl₃): δ 8.33-8.16 (m, 4H), 7.78-7.65 (m, 1H), 7.55-7.46 (m, 4H), 7.38-7.36 (m, 1H), 1.9 (m, 12H, 6CH₂CH₃), 1.3-1.03 (m, 18H, 6CH₂CH₃). ³¹P{¹H} NMR (CDCl₃): δ 16.5. ¹⁹F NMR (CDCl₃): δ -116.5 (m, 2F_{ortho}), -141.5 (m, 2F_{meta}). 5b: Yield: 53 mg (48%). Anal. calcd for C₄₄H₅₃F₄IP₂Pd: C, 55.44; H, 5.60. Found: C, 55.19; H, 5.38. ¹H NMR (300 MHz, CDCl₃): δ 8.33-8.15 (m, 5H), 7.94 (m, 1H), 7.54-7.43 (m, 4H), 7.38-7.30 (m, 2H), 3.05 (t, J = 7.5 Hz, 2H, Per-CH₂), 1.88 (m, PCH₂), 1.79 (m, 2H, Per-CH₂-CH₂-C₄H₉), 1.49 (m, 2H, Per-C₂H₄-C₃H₆-CH₃), 1.37 (m, 4H), 1.15 (m, PCH₂CH₃) 0.92 (t, J = 7.5 Hz, 3H, CH_3). ³¹P{¹H} NMR (CDCl₃): δ 16.5. ¹⁹F NMR (CDCl₃): δ -116.5 $(m, 2F_{ortho}), -141.5 (m, 2F_{meta}).$

trans-[Pd(PerC₆F₄)(PPh₃)₂(NCS)] (6a). KSCN (9 mg, 0.092 mmol) was added to the stirred solution of 5a (0.040 g,

0.046 mmol) in 10 mL of acetone under N₂ atmosphere. After 12 h, the solvent was distilled off, and the residue was redissolved in a minimal amount of dichloromethane, and the cloudy solution was filtered through Kieselguhr. Complex **6a** was precipitated by the addition of hexane (30 mL) as a yellow solid. Yield: 0.035 g, 70%. Anal. calcd for C₆₃H₄₁F₄NP₂PdS: C, 69.52; H, 3.80; N, 1.29. Found: C, 69.13; H, 3.79, N, 1.26. ¹H NMR (300 MHz, CDCl₃): δ 8.22 (m, 4H), 7.77–7.60 (m, 14H), 7.57–7.39 (m, 21H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H). ³¹P{¹H} NMR (CDCl₃): δ 23.8. ¹⁹F NMR (CDCl₃): δ –118.3 (m, 2F_{ortho}), –141.9 (m, 2F_{meta}). IR (KBr, cm⁻¹): 2081 ν (N=C=S).

trans- $[Pd(PerC_6F_4)(PEt_3)_2X]$ (X = Br (7a); X = I (8a)). To a solution of Pt(PEt₃)₄ (0.190 g, 0.285 mmol) in toluene (20 mL) under N2 atmosphere was added PerC6F4Br (for 7a) or $PerC_6F_4I$ (for 8a) (0.285 mmol) and the mixture was stirred for 12 h at room temperature. Then, the solvent was removed in vacuum and the residue was chromatographed on deactivated alumina with CH_2Cl_2 -hexane (2:1) as the eluent. 7a: Yield: 0.060 g, (23%). Anal. calcd for C38H41F4BrP2Pt: C, 50.12; H, 4.54. Found: C, 49.62; H, 3.93. ¹H NMR (300 MHz, CDCl₃): δ 8.26 (m, 4H), 7.73 (m, 2H), 7.60-7.43 (m, 5H), 7.40-7.32 (m, 1H), 1.85 (m, 12H, 6CH₂CH₃), 1.17 (m, 18H, 6CH₂CH₃). ³¹P{¹H} NMR (CDCl₃): δ 13.9 (s, J_{PPt} = 2442 Hz). ¹⁹F NMR (CDCl₃): δ -119.3 (m, 2F_{ortho}, J_{FPt} = 446 Hz), -142.7 (m, 2F_{meta}, J_{FPt} = 104 Hz). 8a: Yield: 0.075 g, (27%). Anal. calcd for C₃₈H₄₁F₄IP₂Pt: C, 47.66; H, 4.31. Found: C, 47.40; H, 4.15. ¹H NMR (300 MHz, CDCl₃): δ 8.25 (m, 4H), 7.72 (m, 2H), 7.60-7.43 (m, 5H), 7.40-7.32 (m, 1H), 1.85 (m, 12H, 6CH₂CH₃), 1.16 (m, 18H, 6CH₂CH₃). ³¹P{¹H} NMR (CDCl₃): δ 33.0 (s, J_{PPT} = 2442 Hz). ¹⁹F NMR (CDCl₃): δ –120.2(m, 2F_{ortho}, J_{FPt} = 426 Hz), -143.1 (m, $2F_{meta}$, $J_{FPt} = 97$ Hz).

X-ray crystal structure analysis

Single crystals of 1, 2a and 6a suitable for X-ray diffraction studies were obtained from slow diffusion of hexane into a dichloromethane solution of the products at -20 °C. Crystals were mounted in glass fibers, and diffraction measurements were made using a Bruker SMART CCD diffractometer with Mo-K_{α} radiation ($\lambda = 0.71073$ Å).⁴⁶ Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω , the total data set being a hemisphere.⁴⁷ Absorption corrections were applied, based on multiple and symmetryequivalent measurements.48 The structures were solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 5).49 All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All the hydrogen atoms, including those involved in hydrogen bonding, were calculated with a riding model. Complex neutral-atom scattering factors were used.⁵⁰ Several peaks of low intensity were found in the structure of compound 2a which, despite repeated attempts, could not be fitted to a chemically sensible model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary

Table 5 Crv	stal data and	structure	refinements	for 1 2	and 6a

Compound	1	2a	6a. CH_2Cl_2
Empirical formula	C32H20CO2O6	C ₃₁ H ₂₀ AuF ₄ N	C ₆₃ H ₄₁ F ₄ NP ₂ PdS
Formula weight	618.34	679.45	1173.29
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	Pccn	$P\bar{1}$
a (Å)	8.818(7)	7.685(3)	11.526(3)
b (Å)	14.019(11)	24.297(8)	12.499(4)
c (Å)	22.704(18)	30.344(10)	20.347(6)
$\alpha(\circ)$	78.851(16)	90	78.327(6)
$\beta(\circ)$	84.38(2)	90	80.155(6)
γ (°)	89.824(19)	90	70.918(6)
$V(Å^3)$	2740(4)	5666(3)	2695.5(14)
Z	4	8	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.499	1.593	1.446
Absorpt.	1.255	5.238	0.598
coefficient (mm ⁻¹)			
F(000)	1256	2624	1192
Crystal size (mm)	0.29 imes 0.21 imes	0.26 imes 0.10 imes	0.28 imes 0.23 imes
• • • •	0.02	0.09	0.20
Theta range for data collection	0.92 to 23.56	1.34 to 26.66	1.03 to 26.43
Reflections	18 633	47 834	23 773
Independent	7968	5939	11 010
Absorption	Multi-scan	Multi-scan	Multi-scan
Max. and min.	1.000 and	1.000 and	1.000 and
transmission factor	0.739836	0.596514	0.786607
Data/restraints/	7968/0/723	5939/0/336	11 010/0/676
Goodness-of-fit on F^2	0.966	1.075	1.028
$R_1 \left[I > 2\sigma(I) \right]$ wR ₂ (all data)	0.0579 0.1735	0.0657 0.2173	0.0572 0.1733

publications with the deposition numbers CCDC-870559 for 1, CCDC-870560 for 2a, and CCDC-870561 for 6a. www.ccdc.cam.

Acknowledgements

We thank the Spanish Ministerio de Economía y Competitividad (CTQ2011-2513 and CTQ2011-23862-C02), the Junta de Castilla y León (Project VA248A11-2), and the Generalitat de Catalunya (grant 2009SGR-1459) for financial support. Computing resources at the Centre de Supercomputació de Catalunya (CESCA) were used through a grant of Fundació Catalana per a la Recerca (FCR).

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