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Facile Incorporation of $Pd(PPh_3)_2Hal$ Substituents into Polymethines, Merocyanines, and Perylene Diimides as a Means of Suppressing Intermolecular Interactions

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Ⓢ *Supporting Information*

ABSTRACT: Compounds with polarizable π systems that are susceptible to attack with nucleophiles at C−Hal (Hal = Cl, Br) bonds react with $Pd(PPh_3)_4$ to yield net oxidative addition. X-ray structures show that the resulting $Pd(PPh_3)_2Hal$ groups greatly reduce intermolecular $\pi-\pi$ interactions. The Pd-functionalized dyes generally exhibit solution-like absorption spectra in films, whereas their Hal analogues exhibit features attributable to aggregation.

Highly polarizable organic π systems can exhibit properties that are relevant to organic electronics and nonlinear optics (NLO). In some cases strong $\pi-\pi$ interactions are desirable, for example, for efficient charge transport within organic semiconductors. In others $\pi-\pi$ interactions can be detrimental; for example, the third-order NLO properties of certain polymethines in dilute solution are promising for all-optical switching (AOS) applications yet are not easily translated to the high-chromophore-density films required because of strong intermolecular interactions that lead to aggregate-like spectra in the solid state.[1] Preventing aggregation and $\pi-\pi$ interactions can also be important for optical limiting,[2] dye-sensitized solar cells,[3] and cases where strong fluorescence is required.[4] Approaches used to preclude aggregation with varying degrees of success include host−guest chemistry[5] and attachment of dendrons[4,6] and other bulky groups to the chromophore.[7]

Here we report an effective and simple method of introducing *rigid* steric bulk around π systems. Specifically, $C(sp^3)$−Hal (Hal = Cl, Br) bonds in a variety of species, including cationic and anionic polymethines, neutral merocyanines, and perylene diimides (PDIs), react with $Pd(PPh_3)_4$ to yield net oxidative addition products. Bulky out-of-plane PPh_3 groups allow these chomophores, which otherwise exhibit strong propensities to aggregate, to be spin-cast into 100 wt % films while generally maintaining absorption spectra similar to those seen for dilute (10−100 μM) solutions.

We recently reported minimizing heptamethine aggregation for third-order NLO applications by attaching bulky, rigid out-of-plane groups to both the polymethine bridge and heterocyclic end moieties.[8] While attempting to use Pd-catalyzed cross-couplings to introduce bulky aryl groups into the central meso positions, we instead obtained the products of oxidative addition of *meso*-Cl-substituted dyes to $Pd(PPh_3)_4$ as stable compounds.

Dyes **1Cl**−**5Cl** (see the Supporting Information (SI) for syntheses) react cleanly with 1 equiv of $Pd(PPh_3)_4$ at room temperature under an inert atmosphere to form **1Pd**−**5Pd**, respectively. The reaction is easily scalable (**5Pd** has been prepared on a 1 g scale), and the products are readily purified by column chromatography or recrystallization. ^{1}H, ^{13}C, and ^{31}P NMR data (see the SI) indicate that the two PPh_3 ligands are *trans* (as shown in Scheme 1) but inequivalent, suggesting that the plane formed by the Pd atom and its ligands is roughly orthogonal to the cyanine π system, with the inequivalence of the two PPh_3 ligands arising from the ^{t}Bu substituent. The $Pd(PPh_3)_2Cl$ dyes are stable toward air in the dark as crystalline solids (no decomposition over 1 year was detectable by NMR spectroscopy); studies of photobleaching in air and thermogravimetric analysis indicated that incorporation of the organometallic fragment does not significantly impair the stability of the chromophores (see the SI).

The crystal structures of **2Cl**, **1Pd**, **5Pd**, and **5′Pd** were determined (Figure 1). The phosphines of the Pd compounds were confirmed to be *trans*, and the dihedral angles between the square plane around Pd and the plane of the polymethine π system were found to be ca. 90° (e.g., 88° for **1Pd**). The structure of **2Cl** (Figure 1a,b) consists of centrosymmetric π

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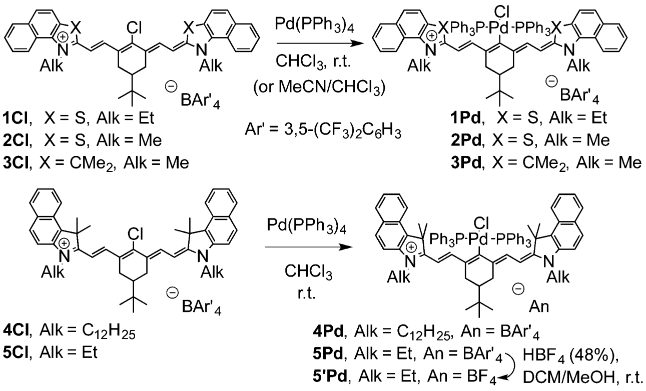
Scheme 1. $Pd(PPh_3)_2Cl$ Functionalization of Heptamethines



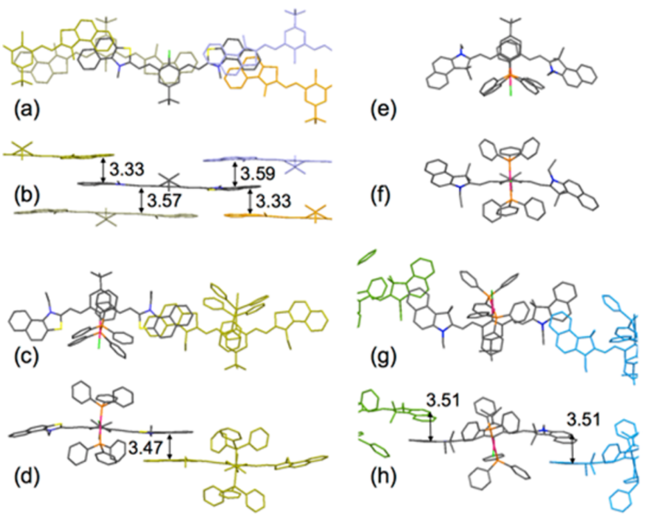
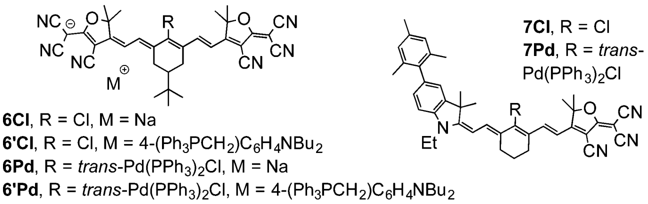


Figure 1. Crystal structures of (a, b) **2Cl**, (c, d) **1Pd**, (e, f) **5Pd**, and (g, h) **5′Pd**, showing for each the interactions of the π system of one polymethine cation (colored by element) with that of its neighbors (uniform colors). Selected interplanar and atom−plane distances in Å are indicated. H atoms, counterions, solvent molecules, and disorder have been omitted for clarity.

dimers; a considerable portion of the π system of each dye is π-stacked with that of its neighbor (3.57 Å average interplanar distance). The terminal rings are also engaged in additional π interactions with those of other cations. The structure of **1Pd** also consists of centrosymmetric π dimers; however, only the naphthalene rings of one of the terminal heterocycles of each dye are involved (3.47 Å interplanar distance). For **5Pd** there are *no* close intermolecular $\pi-\pi$ interactions, perhaps partly because of the out-of-plane CH_3 groups in the terminal heterocycles. The structure of **5′Pd** (Figure 1g,h), in which the BAr'_4 (Ar′ = 3,5-$(CF_3)_2C_6H_3$) anion of **5Pd** is replaced by BF_4, shows the impact of *both* anion and Pd functionalization on π interactions: this structure consists of chains of cations with close π interactions between terminal naphthalene rings.

The reaction is also applicable to a wide range of different polymethines; for example, the anionic cyanine-like dyes **6Pd** and **6′Pd** and the neutral merocyanine **7Pd** (Chart 1) have also been obtained from **6Cl**, **6′Cl**, and **7Cl**, respectively. The crystal structures of **7Cl** and **7Pd** (Figure S1) show that the bulky $Pd(PPh_3)_2Cl$ group also suppresses intermolecular $\pi-\pi$ interactions in the merocyanine.

Chart 1. Anionic and Neutral Polymethines Dyes



Figures 2 and S3 show absorption spectra of Cl- and $Pd(PPh_3)_2Cl$-substituted dyes in solution and as 100 wt % films. The maxima for the $Pd(PPh_3)_2Cl$ species are blue-shifted relative to those of their Cl analogues, suggesting that $Pd(PPh_3)_2Cl$ is a stronger π donor and/or weaker σ acceptor than Cl.[9] The solution fluorescence of **2Pd** is also blue-shifted relative to that of **2Cl** (Figure S5). Their fluorescence quantum yields (QYs) are fairly similar, indicating that the $Pd(PPh_3)_2Cl$ group does not lead to rapid intersystem crossing; indeed, the QY for **2Pd** is ca. 1.5× *larger* than that for **2Cl**.

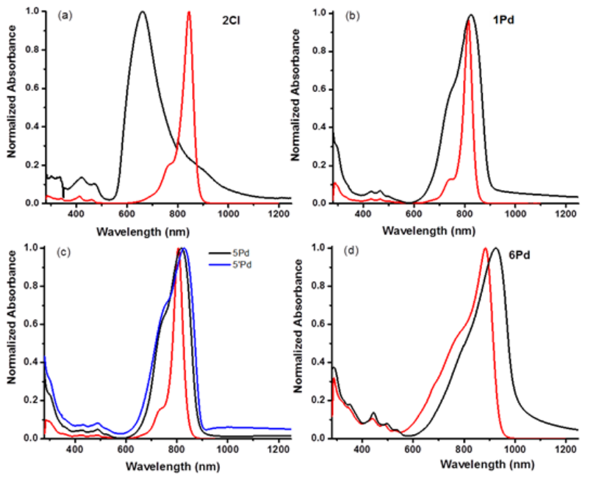


Figure 2. Absorption spectra of (a) **2Cl**, (b) **1Pd**, (c) **5Pd**, and (d) **6Pd** in CH_2Cl_2 solutions (red) and films of 100 wt % dye spin-cast from CH_2Cl_2 blends (black). The blue spectrum in (c) is for a film of 100 wt % **5′Pd** dye spin-cast from CH_2Cl_2.

The absorption spectrum of a 100 wt % film of **2Cl** (Figure 2a) shows a broad high-energy band that is likely due to H-like or low-symmetry aggregates. On the other hand, the interactions in the crystal (Figure 1a,b) more closely resemble those of J-aggregates.[10] Presumably the packing in the spin-cast film differs from that in the crystal; regardless, there are evidently strong interactions between adjacent π systems in both solid environments. The "aggregate" feature is much less prominent and less blue-shifted in the film spectrum of **5Cl** (Figure S3), perhaps as a result of the effect of the CMe_2 portions of the terminal heterocycle. Nevertheless, the spectra of spin-cast films of 100 wt % **1Pd** and **5Pd** (Figure 2b,c) retain more of the characteristic spectral features of polymethines, consistent with the large dye−dye displacements and reduced $\pi-\pi$ interactions induced by the $Pd(PPh_3)_2Cl$ groups in the crystals. However, the spectrum of a neat film of **2Pd** suggests J-aggregation (Figure S3). The absorption spectra of neat films of **5Pd** and **5′Pd** are similar, indicating that in the presence of the bulky $Pd(PPh_3)_2Cl$ groups the anion has relatively little effect (in contrast to 10 wt % films of related Cl dyes[11]).

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Neat films of the anionic dyes **6Pd** and **6′Pd** and neutral merocyanine **7Pd** also exhibit spectra that more closely resemble their solution spectra than do those of their Cl analogues **6Cl**[12] and **7Cl**, although for **6Pd** the solid-state absorption maxima are more red-shifted relative to those in solution than for **6′Pd** (Figures 2d and S3). In view of previous work on **6′Cl** and analogues with different cations,[13] **6Pd** and **6′Pd** provide an opportunity to examine the utility of $Pd(PPh_3)_2Cl$ functionalization for NLO applications; spin-coated films of 50 wt % blends with amorphous polycarbonate (APC) were studied to enable direct comparison to the literature.[13] Poor optical quality (Figure S13) precluded acquisition of reliable data for **6Pd**, but data acquired at 1550 nm for 50 wt % **6′Pd**/APC (Figure S15) and 50 wt % **6′Cl**:APC[13a] are compared in Table 1 along with the linear losses at the same wavelength. The magnitude of $\mathrm{Re}(\chi^{(3)})$ for the **6′Pd**/APC film is comparable to that for APC blends of **6′Cl** and analogues with different counterions,[13a] but the linear and nonlinear optical losses are both significantly lower (the latter corresponding to a larger value of the two-photon figure-of-merit, $|\mathrm{Re}(\chi^{(3)})/\mathrm{Im}(\chi^{(3)})|$), indicating improved suitability for AOS applications.

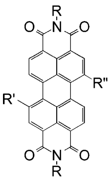
Table 1. NLO Properties of 50 wt % Blends of 6′Cl and 6′Pd with APC at 1550 nm

	6′Cl[13a]	**6′Pd**
$\mathrm{Re}(\chi^{(3)})$ (10^{-11} esu)	−3.8	−4.2
$\lvert\mathrm{Re}(\chi^{(3)})/\mathrm{Im}(\chi^{(3)})\rvert$	2.7	7.2
linear loss (dB cm^{-1})[a]	7.5	5.6

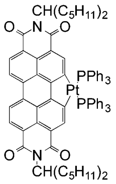
[a] Determined using a prism coupler; the loss for a neat APC film was measured to be ca. 1.9 dB cm^{-1}.

A related conversion of dibromo-PDI **I** to the $Pd(PPh_3)_2Br$ species **II** (Chart 2) using $Pd_2(dba)_3$ and PPh_3 at 50 °C has previously been described.[14] We found that this reaction can also be accomplished using the same conditions as for the polymethines: direct reaction of **PDI-Br₂** and **PDI-Br₁** with $Pd(PPh_3)_4$ at room temperature afforded compounds **PDI-Pd₂** and **PDI-Pd₁**, respectively. $Pt(PPh_3)_4$ also reacts with bromo-PDI derivatives but gives somewhat different products: **PDI-Pt₁**, which contains a *cis*-$Pt(PPh_3)Br$ substituent, and the metallocycle **PDI-cycloPt** were obtained from **PDI-Br₁′** (Chart 2).

Chart 2. Pd and Pt PDI Derivatives



cpd	R	R'	R"
I	cyclohexyl	Br	
II	cyclohexyl	*trans*-$Pd(PPh_3)_2Br$	
PDI-Br₂	$CH_2CHEtBu$	Br	
PDI-Pd₂	$CH_2CHEtBu$	*trans*-$Pd(PPh_3)_2Br$	
PDI-Br₁	$CH_2CHEtBu$	Br	H
PDI-Pd₁	$CH_2CHEtBu$	*trans*-$Pd(PPh_3)_2Br$	H
PDI-Br₁'	$CH(C_5H_{11})_2$	Br	H
PDI-Pt₁	$CH(C_5H_{11})_2$	*cis*-$Pt(PPh_3)_2Br$	H



PDI-cycloPt

The absorption spectrum of a **PDI-Br₂** film is very different from that of **PDI-Br₂** in solution (Figure 3a), as is typical for *N*,*N*′-dialkyl-PDIs without large 1,7-substituents, where π stacking is usually found in crystal structures (e.g., that of **I**[15]). However, the spectra of **PDI-Pd₂** films (Figure 3b) indicates minimal aggregation, consistent with other work on PDIs with large 1,7-substituents, such as 2,6-diphenylphenoxy groups,[7a] and with the effective separation of neighboring PDI cores found in the crystal structure of **PDI-Pd₂** (Figure S2) and also that of **II**.[14] Both the solution and film fluorescence spectra (Figure S5) of **PDI-Pd₂** are consistent with molecule-based emission; the QYs are 0.68 and 0.13, respectively. The structure of **PDI-Pd₁** (Figure S2) consists of slipped π dimers, but films also show a solution-like spectrum (Figure S4). The absorption spectrum of a **PDI-Pt₁** film (Figure S4) indicates stronger aggregation effects than for **PDI-Pd₁**, consistent with less effective prevention of approach of neighboring PDIs by *cis*-PPh_3 ligands. Given the rapid crossing to the triplet manifold seen for Pt−acetylide-functionalized PDIs,[16] studies of the excited-state dynamics of the Pt−PDI dyes are underway.

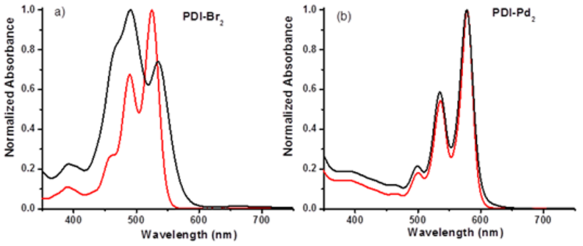


Figure 3. Absorption spectra of (a) **PDI-Br₂** and (b) **PDI-Pd₂** in CH_2Cl_2 solutions (red) and 100 wt % films spin-cast from CH_2Cl_2 (black).

In conclusion, $Pd(PPh_3)_2Hal$ (Hal = Cl, Br) can readily be introduced into a variety of polymethines and PDIs and can effectively suppress the effects of intermolecular interactions on the optical properties in high-chromophore-density films. In contrast to our previous method of minimizing aggregation of chalcogenopyrylium heptamethines,[8] which required multistep synthesis, the dyes obtained here can be readily assembled in a few steps from commercial materials, with the bulky group being introduced in the final step. The reaction of metal−phosphine compounds and C−Hal bonds may prove useful in other areas of organic photonics and electronics where control of aggregation is required.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06361.

Experimental details, decomposition studies, and additional figures showing spectra and crystal structures (PDF)

Crystallographic data for **1Pd**, **2Cl**, **5Pd**, **5′Pd**, **7Cl**, **7Pd**, **PDI-Pd₁**, and **PDI-Pd₂** (CIF)

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Notes

The authors declare no competing financial interest.

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