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Palladium Complexes of Perylene Diimides: Strong Fluorescence Despite Direct Attachment of Late Transition Metals to Organic Dyes

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We prepared the first σ-bonded metal complexes of widely utilized organic dyes, perylene tetracarboxylic acid diimides (PDIs). These 1,7-dipalladium PDI complexes were synthesized by C–Br oxidative addition of 1,7-dibromo-*N*,*N*′-dicyclohexyl PDI (Br_2PDI) to Pd(0) phosphine complexes bearing triphenylphosphine and bischelating 1,2-bis(diphenylphosphino)ethane (dppe). The structures of Pd–PDI complexes were elucidated by single-crystal X-ray analysis. Surprisingly, despite direct attachement of two late transition metal centers, Pd–PDI systems are highly fluorescent ($\Phi = 0.65$ and 0.22 for triphenylphosphine and dppe systems, respectively). This is rationalized in terms of weak electronic interactions between the metal centers and PDI π-system, as revealed by TD-DFT calculations.

Direct attachment of late transition metals to the aromatic systems of fluorescent organic chromophores entails unique structures and photofunction, yet the fluorescence is usually quenched due to efficient intersystem crossing.[1] This is due to enhanced spin−orbit coupling resulting from a heavy-atom effect induced by late transition metals. We show here that metal complexes based on perylene tetracarboxylic acid diimide (PDI) dyes, in which two palladium centers are attached to the dye aromatic core through metal−carbon σ-bonds, are highly fluorescent as a result of relatively weak electronic coupling between the metal-based orbitals and the dye π-system. Direct attachment of late transition metal centers to an organic dye, while maintaining high fluorescence, can represent an efficient tool for creating new structural and functional motifs, significantly augmenting the diversity of available photofunctional systems.

PDIs are widely utilized organic dyes.[2] They demonstrate exceptional thermal and photochemical stability, strongly absorb visible light, and show high fluorescence quantum yields.[3−5] PDIs have been utilized as industrial dyes,[2] electronic materials,[6−9] sensors,[10,11] photovoltaics,[12−16] and building blocks for light-harvesting[17−22] and artificial photosynthetic systems.[23] While a variety of organic groups have been attached to the PDI core at the positions 1, 6, 7, and 12 (bay region),[3] direct attachment of transition metal centers to the PDI aromatic system has not been reported. Metal center and auxiliary ligand choice in such PDI derivatives would allow control over structure, photophysics, and self-

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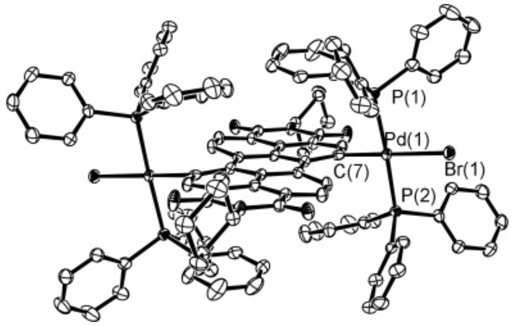
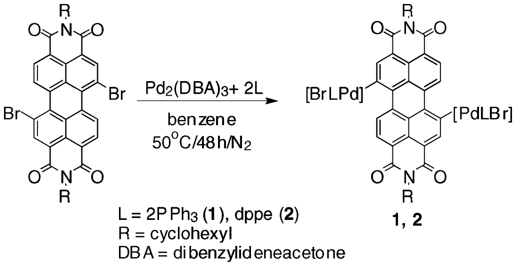


Figure 1. ORTEP drawing of complex **1**, 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(7), 2.019(3); Pd(1)−P(1), 2.3607(8); Pd(1)−P2(7), 2.3550(8); Pd(1)−Br(1), 2.5204(8); C(7)−Pd(1)−Br(1), 179.57(9); P(1)−Pd(1)−P(2), 172.12(3).

organization. We prepared *the first σ-bonded metal complexes of PDI* employing oxidative addition of 1,7-dibromo-*N*,*N′*-dicyclohexyl PDI (Br$_2$PDI)[24] to Pd(0) phosphine complexes prepared in situ (eq 1). We chose triphenylphosphine and bischelating 1,2-bis(diphenylphosphino)ethane (dppe) ligands in order to study how changes in the Pd coordination sphere affect the structure and photophysical properties of Pd−PDI complexes.



(1)

Complexes **1** and **2** were characterized by multinuclear NMR spectroscopy, mass spectroscopy, UV−vis and fluorescence spectroscopy, electrochemistry, elemental analysis, and X-ray crystallography. ^{31}P{^{1}H} NMR spectrum of complex **1** gives rise to a singlet centered at 20.9 ppm, consistent with trans arrangement of the phosphines. In complex **2**, the chelating ligand imposes cis configuration resulting in AX pattern in ^{31}P{^{1}H} NMR spectrum exhibiting doublets at 36.3 and 50.9 ppm (J_{PP} = 28.5 Hz). The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra confirm the different ligand coordination modes in **1** vs **2**. Notably, complexes **1** and **2** are stable for days in aerated solutions.

Further insight into the structure of **1** and **2** was obtained from X-ray crystallography. Single-crystal X-ray studies show that the auxiliary ligands choice has a pronounced effect on the structure, see Figures 1 and 2. X-ray analysis reveals that the phosphines in complex **1** are in a trans configuration, while in complex **2**, these are cis to each other, in agreement with the NMR studies. Complexes **1** and **2** have square planar geometry around the Pd centers. There is no significant change in the bond lengths of the PDI skeletons relative to Br$_2$PDI, whose X-ray structure has been reported.[24] The central six-membered rings of the PDI moieties in **1** and **2** are somewhat less twisted from planarity than in Br$_2$-PDI: the dihedral angles in the bay area are 12.1° and 17.3° for complexes **1** and **2**, respectively, compared to 24° in Br$_2$-PDI.[24] An intramolecular $\pi-\pi$ stacking motif is present in the crystal structures of **1** (four phenyl rings interact with the PDI π-system) and **2** (two phenyl rings interact with the PDI), see Figure 1. Interestingly, the crystal structure of **1** reveals that the PDI moiety is enclosed between the phenyl groups of the phosphine ligands, representing a novel, potentially useful structural motif for crystal engineering of PDI-based materials. Nuclear Overhauser effect (NOE) studies indicate that **1** and **2** do not show NOE attributable to π-stacking in solution.

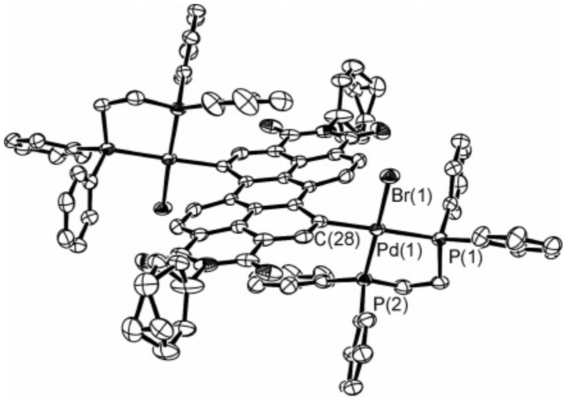


Figure 2. ORTEP drawing of complex **2**, 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(28), 2.053(3); Pd(1)−P(1), 2.3355(9); Pd(1)−P(2), 2.251(1); Pd(1)−Br(1), 2.4980(7); C(28)−Pd(1)−P(1), 171.90(8); Br(1)−Pd(1)−P(2), 172.62(3).

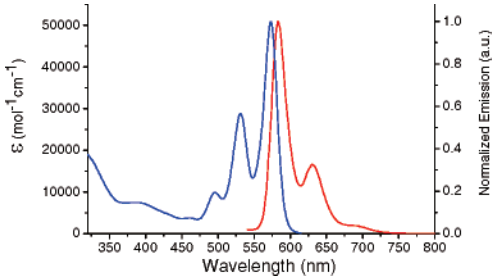


Figure 3. UV−vis (blue trace) and fluorescence (red trace) spectra of complex **1** in dichloromethane. Complex **2** shows very similar spectra.

UV−vis spectra of complexes **1** and **2** show similar absorption bands in dichloromethane peaked at 573 and 572 nm, respectively, with vibronic structure typical for S_0-S_1 transition of PDI chromophores,[3] see Figure 3. It should be noted that the absorption bands of **1** and **2** are red-shifted by ca. 50 nm relative to unsubstituted PDIs ($\lambda_{max} \approx 520$ nm).[3] Such a red-shift indicates that the Pd centers have electron-donating character (e.g., for diphenoxy PDIs, $\lambda_{max} \approx 550$ nm).[3,5] Complexes **1** and **2** show strong luminescence peaked at 584 nm, see Figure 3. The emission quantum yield of complex **1** is 65%, while the quantum yield of complex **2** is 22% in dichloromethane. In a less polar solvent such as benzene, **1** and **2** show absorption and emission spectra similar to those obtained in dichloromethane solution, indicating that the electronic transitions do not have significant charge-transfer character. The emission lifetimes are 7.5 and 2.8 ns for complexes **1** and **2**, respectively. The

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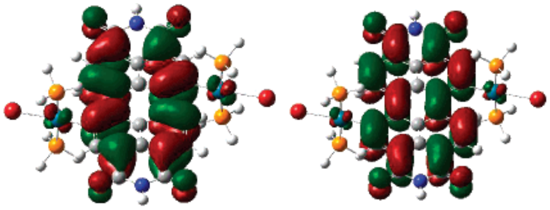

Figure 4. TD-DFT-derived contour surfaces of HOMO (right) and LUMO (left) for model system mimicking complex **1** (H imide substituents, PH_3 ligands).

absorption and emission properties of complexes **1** and **2** remain unchanged in the presence of air. Overall, the position and vibronic structure of the emission peaks of **1** and **2** (small Stokes shifts, mirror image of absorption), independency of the emission on the presence of air, and short lifetimes suggest that the observed emission originates from the first excited singlet states. Femtosecond and nanosecond transient absorption studies employing 572-nm excitation (see Supporting Information) further confirm the formation of a ^{1*}PDI state, revealing its characteristic transient absorption peak in the spectra of **1** and **2**. The decay of ^{1*}PDI results in both fluorescence and intersystem crossing (as evidenced by the rise of PDI triplet bands, the triplet yield is 6% for **1** and 20% for **2**). Thus, our photophysical studies show that the *organopalladium PDIs are highly fluorescent*, unlike most complexes with metals directly attached to aromatic cores of organic chromophores.[1] Surprisingly, a heavy-atom effect is relatively moderate in σ-bonded Pd−PDI complexes, especially in the case of complex **1**.

In order to gain insight into the electronic structure of **1** and elucidate the nature of the heavy-atom effect induced by Pd centers, we performed TD-DFT calculations (B3LYP/SDB-cc-pVDZ//B3LYP/SDD level of theory) on a model system mimicking complex **1**, see Figure 4. Frontier molecular orbitals of the model system, HOMO and LUMO, are both localized on the PDI ligand, with minor participation of the Pd centers in the frontier orbitals makeup. Thus, in complex **1**, σ-bonds connecting two late transition metal centers with the chromophore core do not bring about strong interaction between the Pd orbitals and PDI π-system, localizing the electronic excitation mostly on the PDI ligand. Such electronic structure is expected to diminish the Pd heavy-atom effect.[25,26] Complex **2** demonstrates more efficient intersystem crossing than **1**, most probably because of its different structure and orbital makeup, see Figure 5. The Pd d_{z^2} orbital, participating in the HOMO makeup of **2**, may introduce somewhat stronger electronic coupling between PDI and Pd. Yet, this does not bring about exclusive intersystem crossing, since complex **2** demonstrates a significant fluorescence quantum yield (22%). Notably, Pd−PDI complexes, in which metal centers are bonded through pyridine ligands attached at the PDI imide positions, show fluorescence quantum yields of 88%, indicating that the longer distances and weaker electronic coupling between Pd and PDI further diminish the heavy-atom effect.[18]

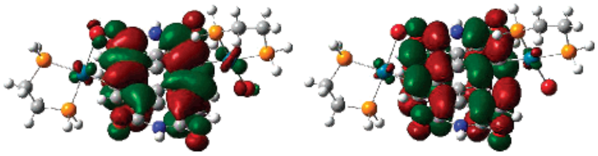

Figure 5. TD-DFT-derived contour surfaces of HOMO (right) and LUMO (left) for model system mimicking complex **2** (H imide substituents, $H_2P-(CH_2)_2-PH_2$ ligands).

In conclusion, the first σ-bonded metal complexes, based on widely utilized in research and industry PDI dyes, have been synthesized and fully characterized. These complexes show unexpectedly strong fluorescence despite the fact that two late transition metals are directly attached to an aromatic system of the organic dye. This effect is due to relatively weak electronic coupling of Pd with the frontier π-orbitals of PDI. The structure and function of such complexes can be controlled by an auxiliary ligand choice. We believe that these findings will allow development of novel photofunctional systems based on PDI and transition metal complexes and provide guidelines for the control over photophysical characteristics of σ-bonded organometallic dyes.

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Supporting Information Available: Experimental and computational details; synthetic procedures and characterization; X-ray data (CIF); time-resolved data. This material is available free of charge via the Internet at http://pubs.acs.org.

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