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Viable access to the triplet excited state in peryleneimide based palladium complex[§]

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Abstract. Triplet excited state in organic chromophores is ubiquitously significant owing to its utility in light harvesting and photovoltaic device applications. Herein, we report the enhancement in the triplet character of an innately triplet deficient peryleneimide chromophore via incorporation of a heavy atom. Palladium incorporated perylenemonoimide (PMI-Pd) was synthesized via oxidative addition of PMI-Br into Pd(0) under inert experimental conditions. The structural sanctity of the PMI-Pd and the model derivative PMI was characterized via single crystal X-ray diffraction and the close-packing was examined employing Hirshfeld surface analysis. The steady-state spectroscopic measurements of PMI-Pd in chloroform reveal an apparent perturbation in the UV-Vis absorption, fluorescence emission and lifetime characteristics. A much higher perturbation is observed in the ultrafast photoexcited processes of PMI-Pd in chloroform as envisaged via nanosecond transient absorption (nTA) measurements. The nTA measurements of PMI-Pd in chloroform reveal a significant enhancement in the triplet character of PMI-Pd as compared to the model derivative PMI. Spin-orbit coupling (SOC) mediated triplet enhancement in PMI-Pd suggest heavy atom incorporation as a viable route for accessing the triplet excited states in triplet deficient aromatic chromophores. SOC mediated triplet enhancement in innately triplet deficient organic chromophores can revive the utility of these materials for novel photovoltaic and energy storage applications.

Keywords. Perylenemonoimide; palladium complex; triplet; spin-orbit coupling.

1. Introduction

Peryleneimide (PI) family of chromophores have been long-known as a lightfast vat dye and have been explored for its versatile optical properties.^{1,2} Owing to its remarkable fluorescence characteristics and high photo, thermal and chemical stability, PI's have gained immense significance in emerging optical and electronic device applications.^{3–5} Additionally, the significant electron affinity of PI fortifies its utility as a nonfullerene acceptor while exploring fundamental aspects of light-harvesting in artificial donor–acceptor (D–A) systems,^{6–8} its application in organic bulk heterojunction solar cells^{9,10} and incipient energy storage application.^{11–13} However, PI vitiates its intense fluorescence character upon self-assembly (viz. solidstate) and is inherently triplet deficient.¹⁴ Long-lived triplet character of a chromophore can be a vital factor controlling the exciton migration and the efficiencies of the D–A blends used for organic photovoltaics.^{15,16} To date, the access to the triplet excited state in organic chromophores has been reported *via* bimolecular triplet sensitization,¹⁷ spin-orbit coupling mediated heavy-atom effect,^{18–21} singlet fission^{14,22,23} and

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charge-recombination of the photoinduced radical-ion pair intermediates.^{24–26} Though the above-mentioned methods can populate the triplet state, they are prone to annihilation and the generation of efficient long-lived triplet excited-state in innately triplet deficient chromophores remains a highly investigated subject.

Our continual efforts in exploring the photoexcited state properties of organic crystalline²⁷⁻²⁹/nonplanar D-A assemblies,³⁰⁻³² and core-twisted^{14,33} organic chromophores motivated us to investigate the effect of a heavy-atom on the photoexcited state properties of perylenemonoimide (PMI). The synthesis of the heavyatom appended PMI (PMI-Pd) was carried via oxidative addition of PMI-Br to Pd(PPh₃)₄ under inert experimental conditions. The structure of PMI-Pd was further characterized via nuclear magnetic resonance (NMR), high-resolution mass spectrometry (HRMS) and single crystal X-ray diffraction analysis. The consequence of the direct attachment of the -Pd(PPh₃)₂Br to the PMI core was evident from the stead-state spectroscopic and time-resolved lifetime analysis. The UV-Vis absorption and fluorescence emission spectra of PMI-Pd in chloroform reveal an apparent red-shift as compared to the model derivative. The lifetime analysis of PMI-Pd in chloroform also displayed a similar perturbation as compared to the model derivative PMI. The effect of the heavy-atom (Pd) substitution in PMI was further explored employing the time-resolved spectroscopic analysis. The femtosecond transient absorption (fTA) measurements of both PMI-Pd and the model derivative PMI reveal the presence of the singlet excited state at 630-640 nm. The nanosecond transient absorption (nTA) measurements of PMI-Pd and PMI reveal the presence of the triplet excited state; however, the singletto-triplet transition was not perceived. Interestingly, the triplet formation in PMI-Pd was found to be higher (0.58 ± 0.01) as compared to the model derivative PMI (0.08 ± 0.005) leading to the quenching of the fluorescence in PMI-Pd. A similar heavy-atom (Pd) substituted PDI derivative displayed a high fluorescence character and a comparatively low yet significant heavy-atom effect upon direct attachment of Pd to the PDI core.⁶ The quenched fluorescence in PMI-Pd and the higher yield of triplet formation suggest the combined effect of the heavy atoms (Pd and the adjacent Br) mediating the spinorbit coupling in PMI-Pd. Thus, the spin-orbit coupling mediated heavy-atom can allow a viable access route to achieve triplet character in integrally triplet deficient aromatic chromophores. Triplet enhancement in PMI-Pd as compared to the triplet deficient PMI chromophore can renovate the utility of such chromophoric systems for innovative light harvesting and energy-related applications.

2. Experimental

2.1 Materials and methods

All chemicals were obtained from commercial suppliers and used as received without further purification. All reactions were carried out in oven-dried glassware prior to use and wherever necessary, were performed under dry nitrogen in dried, anhydrous solvents using standard gastight syringes, cannulae, and septa. Solvents were dried and distilled by standard laboratory purification techniques. TLC analysis was performed on precoated aluminium plates of silica gel 60 F254 plates (0.25 mm, Merck) and developed TLC plates were visualized under short and long wavelength UV lamps. Flash column chromatography was performed using silica gel of 200-400 mesh employing a solvent polarity correlated with the TLC mobility observed for the substance of interest. Yields refer to chromatographically and spectroscopically homogenous substances. Melting points were obtained using a capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR spectrometer as KBr pellets. ¹H and ¹³C NMR spectra were measured on a 500 MHz Bruker Avance DPX spectrometer. Internal standard used for ¹H and ¹³C NMR is 1.1.1.1-tetramethyl silane (TMS). High-resolution mass spectra (HRMS) were recorded on Thermo Scientific Q Exactive mass spectrometer using electrospray ionization (ESI, positive mode) technique.

2.1a *Steady-state* spectroscopy: Photophysical measurements of the derivatives were carried out in a cuvette of 3 mm path length unless otherwise mentioned. Absorption and emission spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR and Horiba Jobin Yvon Fluorolog spectrometers respectively. Solution-state relative quantum yield measurements were performed using Rhodamine 6G as the standard (λ_{ex} = 488 nm, reported quantum yield $\Phi_f = 0.94$).³⁴ Lifetime measurements were carried out in an IBH picosecond time-correlated single photon counting (TCSPC) system. The fluorescence decay profiles were de-convoluted using IBH data station software (DAS 6.3), and fitted with exponential decay, minimizing the χ^2 values.

Solution-state fluorescence quantum yields of PMI and PMI-Pd derivatives were calculated by relative quantum yield method as follows,

$$\Phi_{\rm s} = \Phi_{\rm ref} \left(\frac{\rm I_s}{\rm I_{\rm ref}}\right) \left(\frac{\rm OD_{\rm ref}}{\rm OD_s}\right) \left(\frac{\rm n_s}{\rm n_{\rm ref}}\right)^2 \tag{1}$$

wherein, Φ_s and Φ_{ref} are the quantum yields of sample and reference respectively, I_s and I_{ref} are the area under the emission spectrum for sample and reference respectively. OD_s and OD_{ref} are the absorbances of the sample and reference respectively at the excitation wavelength. n_s and n_{ref} are the refractive index of the solvent in which sample and reference are taken.

Parameters	PMI-Pd
Formula	C ₇₀ H ₅₆ BrNO ₂ P ₂ Pd
Formula wt	1191.40
Colour, shape	Red
Dimens, mm	$0.24 \times 0.1 \times 0.08$
Crystal system	Triclinic
Space group, Z	P - 1
a, Å	13.1460
b, Å	14.7260
c, Å	19.047
α, deg	110.927
β, deg	91.113
γ, deg	102.763
V, Å ³	3339.3
Temp, K	296 (2)
d _{calcd} , mg/m ³	1.185
No. of reflections collected	50862
No. of unique reflections	11666
$2 \theta_{\text{max}}$, deg	50
No. of parameters	694
R1, wR2 $(I > 2s(I))$	0.0915, 0.2737
R1, wR2 (all data)	0.1352, 0.3227
Goodness of fit	1.096
CCDC number	1845450

Table 1. Crystallographic data and refinementparameters for crystalline PMI-Pd.

The crystal structure of PMI is available on CCDC with a deposition number 900321.²⁷

2.1b X-ray crystallography: Single crystal of PMI-Pd was obtained by slow evaporation of solvent from *n*-hexane: chloroform (1:1) homogenous mixture at room temperature. High-quality specimens of approximate $0.24 \times 0.1 \times$ 0.08 mm³ dimension were selected for the X-ray diffraction experiments. Crystallographic data collected for PMI-Pd is presented in Table 1. A single crystal was mounted using oil (Infineum V8512) on a glass fibre. All measurements were made on a CCD area detector with graphite monochromated Mo K_{α} radiation. The data were collected using a Bruker APEXII detector and processed using APEX2 from Bruker. The structure was solved by a direct method and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELX-97.³⁵ All the programs used during the crystal structure analysis are incorporated in the WINGX software.³⁶ The full validation of CIF and structure factor of PMI-Pd was performed using the checkCIF utility and found to be free of major alert levels. 3D structure visualization and the exploration of the crystal packing of PMI-Pd was carried out using Mercury 3.5.1.37,38

2.1c Femtosecond transient absorption (fTA) technique: Spectra-Physics Tsunami Oscillator (80 MHz, 800 nm) was used as a seed for a Spectra-Physics Spitfire Regenerative Amplifier (1 kHz, 4 mJ). A fraction of the amplified output was used to generate 400 nm pump pulse. Residual 800 nm pulse was sent through a delay line inside an Excipro pump-probe spectrometer from CDP systems. A rotating CaF₂ plate (2 mm thickness) was used to generate a continuum of white light from the delayed 800 nm pulses. The continuum of white light was split into two and the streams were used as a probe and reference pulses. Transient absorption spectra were recorded using a dual diode array detector having a 200 nm detection window with an optical delay of 1.6 fs. Sample solutions were prepared in a rotating sample cell with 4 mm path length. IRF was determined by solvent (10% benzene in methanol) two-photon absorption and was found to be approximately 110 fs at about 530 nm. Energy per pulse incident on the sample is attenuated employing 80% neutral density filter when required. fTA measurements of PMI and PMI-Pd in CHCl₃ were excited at 400 nm, 200 nJ, \approx 110 fs pulses, to moderate singlet-singlet annihilation that occurs often in multichromophoric assemblies.³⁹ The observed kinetic components are laser intensity independent, ruling out the assignment of kinetic components to singletsinglet annihilation.³⁹

2.1d Nanosecond absorption transient (nTA)measurements: Nanosecond laser flash photolysis experiments of the argon-purged solutions of PMI and PMI-Pd were carried out in an Applied Photophysics Model LKS-60 laser kinetic spectrometer using the second harmonic $(\lambda_{ex} = 355 \text{ nm}, \text{ pulse duration } \approx 7 \text{ ns})$ of a Quanta Ray INDI-40-10 series pulsed Nd: YAG laser as the excitation source. Triplet states of PMI and PMI-Pd in chloroform were confirmed performing the experiments with oxygen purged solutions. Triplet quantum yields upon direct photoexcitation (355 nm) were determined using [Ru(bpy)]Cl₂ in methanol as standard with nonsaturating laser intensities. An equal volume of 0.2 mM solution of β -carotene was added to optically matched solutions of reference and the sample. The equation for the triplet quantum yield is given by, 40

$$\Phi_T^s = \Phi_T^{Ref} \times \frac{\Delta A^s}{\Delta A^{Ref}} \times \frac{k_{obs}^s}{k_{obs}^s - k_0^s} \times \frac{k_{obs}^{Ref} - k_0^{Ref}}{k_{obs}^{Ref}}$$
(2)

Where, Φ_T^s and Φ_T^{Ref} denote the triplet quantum yield of the sample and reference respectively; ΔA^s and ΔA^{Ref} are transient absorption intensity of β -carotene in sample and reference respectively; k_{obs}^s and k_0^s are decay rate of sample transient species before and after the addition of β -carotene. k_{obs}^{Ref} and k_0^{Ref} are the decay rate of reference transient species before and after the addition of β -carotene.

The triplet formation rates in the two derivatives PMI and PMI-Pd were not perceived as the fTA experiments were limited to 2.7–3.5 ns, whereas the nTA measurements provide the signals from 10 ns onwards only. Lack of clear singlet-triplet (S-T) transition in the femtosecond (fTA) and nanosecond transient absorption (nTA) measurements suggest the triplet formation is slow and may form in 3.5–10 ns window, which we are not able to perceive in our current experimental setup.



Scheme 1. Synthesis scheme for PMI-Pd. (a) 2,6-diisopropylamine, imidazole, $Zn(OAc)_2$, H_2O , 190 °C, 24 h; (b) Br₂, I₂, Glacial acetic acid, RT, 6 h; (c) Pd(PPh₃)₄, 2 M K₂CO₃, Toluene, 110 °C, 24 h.

2.1e *Computational analysis*: The vertical excitation energies and harmonic oscillator frequencies of PMI and PMI-Pd were computed using density functional theory (DFT) at the Becke's three parameter functional in combination with the Lee-Yang-Parr correlation functional (B3LYP) and 3-21G basis set. All the computations were performed using the *Gaussian 09 Rev. A.02* and visualized using *GaussView 5.0.*⁴¹

2.1f *Hirshfeld analysis*⁴²: Important intermolecular interactions within the crystal structure of PMI and PMI-Pd were identified through Hirshfeld surface analysis using Crystal Explorer17.⁴³ The Hirshfeld surface is defined as a set of points in 3D space where the ratio of promolecule and procrystal electron densities is equal to 0.5. The exploration of intermolecular contacts is provided by mapping normalized contact distances (d_{norm}), which is a function of the closest distance from the point to the nuclei interior (d_i) and exterior (d_e) to the surface as well as on the van der Waals radii (r_{vdw}). 2D fingerprint which was generated by deriving from the Hirshfeld surface by plotting the fraction of points on the surface as the function of d_i and d_e which provide a visual summary of intermolecular contacts within the crystal.

2.2 Synthesis and structural analysis

Synthesis of PMI and PMI-Br were carried out following our previous reported procedures.^{27,44} The synthesized PMI-Br was further reacted with tetrakis(triphenylphosphine) palladium(0) and 2 M K₂CO₃ solution in toluene (under inert conditions) at 110 °C for 24 h to yield the title compound PMI-Pd (Scheme 1). Red single crystals of PMI-Pd (1:1, *n*hexane: chloroform) was obtained by slow evaporation of solvent from the homogenous solution at room temperature. Crystal structure of PMI is available with CCDC (Deposition No. 900321) and the crystallographic data for PMI-Pd derivative (1845450) is tabulated in Table S1, Supplementary Information (SI).

2.3 Spectral characterization

PMI-Pd: Yield: 10% (dark red solid); M.p. > 300 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.51 (d, J = 8.1 Hz, 1H), 8.45



Figure 1. Molecular structure and close-packing of (a) PMI and (b) PMI-Pd. For clarity, the hydrogens have been omitted in the crystal structure and the close-packing.

(d, J = 8.1 Hz, 2H), 8.18 (d, J = 8.2 Hz, 1H), 8.0–8.02 (m, 2H), 7.44–7.47 (m, 12H), 7.37–7.41 (m, 3H), 7.25 (d, J = 7.85 Hz, 2H), 7.12–7.14 (m, 8H), 7.05–7.08 (m, 12H), 2.66–2.70 (m, 2H), 1.11 (m, 12H); HRMS (ESI): m/z calculated for C₇₀H₅₆BrNO₂P₂Pd [M+H]⁺: 1190.2083; Found : 1190.1963.

3. Results and Discussion

3.1 Synthesis and structure

The title compound PMI-Pd was synthesized by reacting PMI-Br^{27,44} and tetrakis(triphenylphosphine)palladium (0) in toluene (with 2 M K₂CO₃) under inert conditions (Scheme 1, Figure 1). The precursor 9-bromopervlene monoimide (PMI-Br) was synthesized in accordance with our previous reported procedure by reacting pervlene-3,4,9,10-tetracarboxylic anhydride (PTCDA) with 2,6-diisopropylaniline (yielding PMI) followed by successive bromination in the presence of elemental bromine (Scheme 1).^{27,44} Slow evaporation of a solution of PMI (chloroform)²⁷ and PMI-Pd (in 1:1, *n*-hexane:chloroform) afforded decent quality crystals for X-ray diffraction (Figure 1). The molecular structure of PMI and PMI-Pd suggest a steric congestion mediated near-orthogonal ($\theta = 85.8^{\circ}$ and 86.8° respectively) nature of the 2,6-diisopropylphenyl substituent at the imide region (Figure 1). The closepacking in PMI reveals the presence of two non-identical stacked PMI dimers with a distance of 3.33 and 3.34 Å. In contrast, the close-packing in PMI-Pd reveals the steric intervention of the flanking triphenylphosphine moiety between the two PMI cores lending a virtually negligible π -overlap (7.57 and 7.73 Å) between the adjacent PMI-Pd dimers (Figure 1). To get additional insights into the subtle intermolecular interactions guiding the close-packing, Hirshfeld surface analysis of PMI and PMI-Pd was carried out. Hirshfeld surface analysis and the corresponding 2D finger plot quantifies the % intermolecular interactions in the molecular assembly of PMI and PMI-Pd (Table S1, Supplementary Information). The ρ (%C•••H/%C•••C) value obtained from the Hirshfeld analysis suggest a β -motif and herringbone arrangement in the crystalline assembly (Figures S1-S2, Table S1, in Supplementary Information) of PMI and PMI-Pd, respectively.

3.2 Steady-state spectroscopy

To evaluate the preliminary photophysical features of PMI and PMI-Pd, steady-state UV-Vis absorption, fluorescence emission and lifetime measurements were carried out in chloroform (Figure 2). The UV-Vis absorption of PMI reveals a broad absorption ranging from 400 to 590 nm with peak centered at 520 nm (Table 2). The observed UV-Vis absorption of PMI in chloroform corresponds to a typical π - π * (HOMO \rightarrow LUMO) transition similar to the earlier literature reports (Figure 3, Table S2, in Supplementary Information).^{1,44} The fluorescence spectrum ($\lambda_{ex} = 480$ nm) of PMI in chloroform reveal an intense emission ($\Phi_f = 0.86 \pm$ 0.02) with a narrow Stokes' shift and a characteristic vibronic pattern archetypally seen in rylene chromophores.⁴⁵ The fluorescence lifetime measurement of PMI reveals a monoexponential decay with a lifetime of 4.85 ns suggesting a single decay pathway for the singlet excited state. The UV-Vis absorption spectrum of PMI-Pd complex reveals a red-shifted (20-30 nm) absorption centered at 540 nm (HOMO \rightarrow LUMO) while still maintaining the characteristic vibronic features (Figure 3, Table S2, in Supplementary Information). The red-shifted UV-Vis absorption in PMI-Pd can be a result of the perturbation exerted by the $-Pd(PPh_3)_2Br$ on the PMI core.^{1,46} A much higher perturbation is observed in the fluorescence spectrum ($\lambda_{ex} = 480$ nm) of PMI-Pd in chloroform as compared to bare chromophore PMI. The emission spectrum of the PMI-Pd in chloroform reveals a 60 nm red-shift and a concomitant decrease in the fluorescence quantum yield ($\Phi_f = 0.38 \pm 0.02$) as compared to PMI. Moreover, the picosecond timeresolved lifetime analysis of PMI-Pd in chloroform reveal a bi-exponential decay ($\tau_{\rm f} = 1.64$ and 4 ns) of the fluorescence emission. The quenched emission and the bi-exponential decay of the fluorescence emission suggest an alternate pathway/phenomenon for the decay of the singlet excited state via incorporation of the Pd moiety in PMI-Pd. The photoexcited state characteristics of crystalline PMI and PMI-Pd differed slightly from the solution state properties (Figure S3 and Table S3, in Supplementary Information). The UV-Vis absorption of crystalline PMI (300-650 nm) and PMI-Pd (300-750) reveal red-shift as compared to that



Figure 2. (a) Absorption and emission spectra ($\lambda_{ex} = 480 \text{ nm}$) of PMI (top) and PMI-Pd (bottom); fluorescence decay profiles of (b) PMI ($\lambda_{ex} = 439 \text{ nm}$, pulse width < 100 ps; $\lambda_{emi} = 531 \text{ nm}$) and (c) PMI-Pd ($\lambda_{ex} = 478 \text{ nm}$, pulse width < 90 ps; $\lambda_{emi} = 600 \text{ nm}$).

Table 2. Photophy	ysical properti	es of PMI and	l PMI-Pd in	$CHCl_3$.
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Derivative	$\lambda_{abs} \; (nm)$	λ_{f} (nm)	$\tau_{f} \; [\text{amplitude}] \; (ns)$	Φ_{f}	τ_T (ns)	Φ_T
PMI PMI-Pd	520 540	539, 578, 636 614, 658, 733	4.85 [100] 1.64 [10.5] 4 [89.5]	$\begin{array}{c} 0.86 \pm 0.02 \\ 0.38 \pm 0.01 \end{array}$	$\begin{array}{c} 1.58 \pm 0.05 \ \mu s \\ 0.90 \pm 0.03 \ \mu s \end{array}$	$\begin{array}{c} 0.08 \pm 0.005 \\ 0.58 \pm 0.01 \end{array}$



Figure 3. The frontier molecular orbital analysis (B3LYP/3-21G) of PMI (left) and PMI-Pd (right), respectively, carried out in *Gaussian 09*.

observed in chloroform solution. The emission spectra of crystalline PMI and PMI-Pd revealed a similar redshifted trend as that of UV-Vis absorption. Interestingly, the picosecond time-resolved lifetime analysis of crystalline PMI-Pd reveal a faster decay of the excited state as compared to crystalline PMI. The faster decay of the fluorescence lifetime in crystalline PMI-Pd suggests an alternate pathway (possibly triplet excited state) responsible for the faster decay of the singlet excited state in PMI-Pd, which is not present in crystalline PMI (Table 2).

3.3 *Transient absorption spectroscopy*

To further probe the photoexcited-state processes in PMI and PMI-Pd, ultrafast transient absorption spectroscopic measurements were carried out in monomeric chloroform solution. The fTA ($\lambda_{ex} = 400$ nm) spectra of PMI and PMI-Pd reveal positive signal at 630–640 nm, suggesting the presence of singlet excited state which does not completely decay within the given experimental window and is further supported by the time-resolved fluorescence lifetimes (Table 2, Figure S4, in Supplementary Information). Though the fTA spectra of PMI and PMI-Pd suggest the presence of the singlet excited state, the singlet-to-triplet conversion was not perceived.

To probe the existence of the triplet excited state, nTA spectroscopic measurements ($\lambda_{ex} = 355$ nm) of PMI and PMI-Pd were carried out in a nitrogen purged chloroform solutions (Figure 4). The nTA spectra of PMI in chloroform reveal positive transient absorption at 500-600 with a peak centered at 560 nm and which decay in a few microseconds timescale ($\tau_T = 1.58 \pm 0.05 \,\mu s$, Figure 4a). The long decay time of the transient species centered at 560 nm suggests the possibility of a triplet excited state. To confirm the existence of a triplet excited state, the nTA measurements of PMI were carried out in oxygen purged solutions. The triplet-triplet energy transfer (from ³PMI-Pd* to the ground state (triplet) of oxygen) mediated decrease in the optical density and the fast decay of the 560 nm component in the oxygen purged solution confirms the presence of the triplet excited state of PMI. On the other hand, nTA measurements ($\lambda_{ex} = 355$ nm) of PMI-Pd in chloroform reveals a transient signal at 620 nm with a lifetime of $0.90 \pm 0.05 \ \mu s$ (Figure 4b). The minor variation in the position of the triplet excited state in PMI-Pd can be due to the difference in the triplet energy levels of PMI-Pd as compared to PMI, arising from a consequence of the incoming $-Pd(PPh_3)_2Br$ (Figure 5). Upon oxygen purging, the positive transient absorption at 620 nm shows an apparent quenching, confirming the species to have a triplet origin. Interestingly, the triplet quantum yield ($\phi_T = 0.58 \pm$ 0.01 µs) of PMI-Pd in chloroform reveal a considerable increment as compared to PMI ($\phi_T = 0.08 \pm$ $0.005 \ \mu$ s). The apparent increase in the triplet yield in PMI-Pd can be a direct consequence of the spinorbit coupling mediated enhanced population of the triplet excited state and the reduced energy difference/near iso-energetic nature of the S_1 and T_2 energy levels (Figure 5). We believe that a tacit understanding of the spin-orbit coupling-mediated heavy-atom effect and the consequent enhancement in the triplet excited state of polyaromatic hydrocarbon can revive the design principles of novel organic materials for optoelectronic applications (Table S4, Supplementary Information).



Figure 4. 2D plot (top) and nTA spectra (bottom, $\lambda_{ex} = 355$ nm) of nitrogen purged solutions of (a) PMI and (b) PMI-Pd; nTA spectra ($\lambda_{ex} = 355$ nm) of oxygen purged solutions of (c) PMI and (d) PMI-Pd.



Figure 5. Jablonski diagram depicting the energy levels and the photophysics of PMI and PMI-Pd.

4. Conclusions

In summary, we report a novel arene-metal conjugate wherein the spin-orbit coupling mediated heavy atom effect conveys a higher triplet population in PMI-Pd. The arene-metal conjugate was synthesized *via* oxidative addition of PMI-Br into Pd(PPh₃)₄under inert conditions. The structural characterization of the model derivative PMI and PMI-Pd were carried out using single crystal X-ray diffraction and the close-packing

analysis revealed the weak intermolecular interactions guiding the three-dimensional packing in the crystalline assembly. The steady-state UV-Vis absorption and emission spectra of PMI-Pd display an apparent red-shift when compared to the model derivative PMI, from a consequence of the effect exerted by the incoming -Pd(PPh₃)₂Br group. The effect of the incoming Pd group is more pronounced in the photoexcited state processes of PMI-Pd. The nTA spectra of PMI-Pd exhibits an apparent increase in the triplet population from the incorporation of the heavy atom (Pd). The spin-orbit coupling-mediated heavy atom effect proposes a viable route to access the triplet excited state in polyaromatic chromophores possessing negligible triplet character. Enhancement of the triplet character in aromatic chromophores can have a progressive impact on the efficacy of such aromatic chromophores in solar light-to-energy conversion applications.

Supplementary Information (SI)

Crystallographic data for the structural analyses of PMI and PMI-Pd have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC Nos. 900321 and 1845450, respectively. Copies of this information are available on request at free of charge from CCDC, Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk). Details of Hirshfeld analysis and close-packing (Figures S1–S2, Table 1), TD-DFT energy levels (Table S2) and fTA (Figure S4) analysis. Supplementary Information is available at www.ias.ac.in/chemsci.

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