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Palladium(II) N-heterocyclic allenylidene complexes with



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Extended intercationic Pd···Pd contacts of 3.30 Å in the crystal structure and distinct MMLCT transitions absorbing at 528 nm and emitting beyond 600 nm in solutions have been revealed with cyclometalated Pd(II) *N*-heterocyclic allenylidene complexes. The Pd(II)-based MMLCT excited states are responsive to concentration, temperature, mechanic force and organic vapors.

Metal-metal-to-ligand charge-transfer (MMLCT) excited states of square planar d⁸ metal complexes, derived from dispersion metal-metal interactions, have attracted much research endeavour.¹ Pt(II) complexes containing dimeric or extended Pt…Pt interactions and low-lying π^* orbitals usually exhibit d σ^* - π^* electronic transitions and triplet MMLCT phosphorescence that is much red-shifted from that of the monomeric species.² In contrast, metallophilic interaction in Pd(II) complexes is highly distance-demanding due to the more restrained and lower-lying 4dz² orbital when compared with the 5dz² orbitals of Pt(II).³ Although Pd(II) complexes with crystallographically determined intermolecular Pd...Pd contacts in the range of 3.3–3.5 Å are scattered in the literature,⁴ so far distinct spectroscopic evidences for excited states with $\mathsf{Pd} \cdots \mathsf{Pd}$ parentage remain elusive. In 2013, Albuquerque, Fernández and co-workers ascribed a 371 nm band in the absorption spectrum of oligophenyleneethynylene-based Pd(II) pyridyl complexes to a supramolecular aggregation involving Pd…Pd interactions.⁵ In 2018, Che and co-workers provided evidences that pincer Pd(II) isocyanide complexes display an MMLCT absorption transition at 439 nm and a triplet MMLCT emission at 540 nm upon supramolecular polymerization assisted by Pd…Pd interactions.6 In the current work, we report that cyclometalated Pd(II) N-heterocyclic allenylidene (NHA) complexes show extended intercationic Pd…Pd contacts in the crystal structure and distinct MMLCT transitions absorbing at 528 nm and emitting beyond 600 nm in solutions. The luminescent mechanochromic and vapochromic properties of the Pd(II) NHA complexes have also been studied.



Scheme 1 Synthesis of complexes **1a–1c**. Reaction conditions: a) Ag_2O , CH_3CN ; b) sulphate-type anion exchange resin, CH_3OH ; c) sodium 2,3,4-tris(dodecyloxy)benzenesulfonate, CH_2CI_2 .

Acyclic allenylidene complexes of Ir(III),⁷ Pt(II),⁸ and Au(III)⁸ complexes luminescent in fluid solutions and in the solid state have been reported recently. In 2009, Bertrand and co-workers reported the isolation of the first Ag(I) NHA complex and the subsequent transmetalation reactions from Ag(I) to Pd(II) and Ru(II).⁹ In 2011, Che, Lu and co-workers revealed a Au(I) NHA complex aggregating in water into a phosphorescent chromonic mesophase.¹⁰ We thus envisage that the balanced σ -donation and π -back bonding interactions and the less steric bulkiness of NHA when compared with N-heterocyclic carbene (NHC) could facilitate Pd…Pd contacts in Pd(II) NHA complexes.

The tridentate cyclometalated Pd(II) NHA salt **1a** was prepared by a reaction between 2-ethynyl-1,3-dimethyl-1*H*imidazol-3-ium⁹ hexafluorophosphate and [(C^N^N)PdCI] (HC^N^N = 6-phenyl-2,2'-bipyridine)¹¹ in the presence of a stoichiometric amount of Ag₂O (Scheme 1). The subsequent anion metathesis with sulphate-type ion-exchange resin¹² and with sodium 2,3,4-tris(dodecyloxy)benzenesulfonate¹³ gave **1b** and **1c**, respectively. All these complexes are solid stable

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checked by a variety of spectroscopic methods including IR, the multi-nuclear NMR, and high-resolution MS (See supporting resolution for details). The ¹³C-NMR signals for C_β in **1a** is at state state

towards air and moisture. The identities of the complexes were



contributes to the Pd(II)-NHA ligation (Scheme 1).

Fig. 1 Packing diagrams of (a) 1a and (b) 1a·DMF in the crystal structures. Solvated DMF molecules are omitted for clarity. Micrographs of crystals of (c) 1a and (d) 1a·DMF under a fluorescence microscope and (e) the corresponding emission spectra recorded with a fluorimeter coupled to the microscope.

Complex 1a crystallized into two pseudo-polymorphs both in triclininc P-1 space group but with contrasting colours. The yellow blocks obtained from an acetonitrile solution shows head-to-head dimeric π - π stacking with a interplanar distance of ca. 3.4 Å and a shortest intermetal distance of 4.965 Å (Fig. 1a). The red needles grown in a DMF/diethyl ether mixture containing solvated DMF molecules shows polymeric head-totail packing with intermetal distances alternating between 3.295 and 3.298 Å along the crystallographic b-axis (Fig. 1b). These Pd---Pd distances are slightly longer than the sum (3.26 Å)¹⁴ of the van der Waals radii of two palladium atoms, are much shorter than those recently reported for the pincer Pd(II) isocyanide complexes (3.34 and 3.37 Å),⁶ and is the shortest ever reported for infinite chain-like cationic Pd(II) complexes without bridging ligands. The C_{α} - C_{β} distance is 1.214 and 1.188 Å for the yellow and red form, respectively, which is slightly longer than that for 2-ethynyl-1,3-dimethyl-1H-imidazol-3-ium (1.181 Å),9 and is within the reported range (1.19-1.24 Å) for typical metal-NHA complexes.7-10

To correlate the crystal structures and the corresponding solid-state emissions, the micrographs (Fig. 1c and 1d) and the emission spectra (Fig. 1e) of the two pseudo-polymorphs of **1a** were synchronically recorded on a fluorescence microscope coupled to a spectrofluorimeter with optical fibres. The yellow blocks (**1a**) showed vibronically structured emission at a peak maximum at 528 nm, whileas the red needles (**1a**·DMF), structureless emission at 611 nm. The polymorph containing infinite Pd…Pd chains obviously red-shifted the solid state emission energies. In addition, the collected bulky powder samples of **1a** and **1b** were exclusively red in color and emitted at peak maximum (lifetime, quantum yield) of 695 nm (1.2 μ s, 43%) and 655 nm (0.27 μ s, 29%), respectively. We hence inferred that the infinite Pd…Pd chains were kept in the bulky solid of **1a** and **1b**.

Complex **1c** displayed luminescent mechanochromic¹⁵ and vapochromic¹⁶ properties at room temperature. Complex **1c** could be isolated as a bright-yellow solid by precipitation in methanol or as a red solid by evaporation of the toluene solution to dryness. Grinding the yellow solid in a mortar (Fig. 2a) or fuming the yellow solid with toluene vapour (Fig. 2b) gave a red-coloured solid. Fuming the red form with methanol vapour gave an orange-coloured solid which reversed to the red form in toluene vapour. The yellow form can only be restored by grinding the red or the orange forms in methanol (Fig. 2b). At room temperature, the yellow, the orange, and the red form emitted at peak maximum (lifetime, quantum yield) of 554 nm (0.48 μ s, 14%), 596 nm (0.73 μ s, 20%), and 633 nm (0.45 μ s, 47%), respectively (Fig. 2c).



Fig. 2 (a) Micrographs of the yellow form of 1c under a 365 nm UV lamp before and after mechanic grinding. (b) A schematic depiction of reversible emission colour change of 1c treated by mechanic grinding and vapour fuming. (c) Emission spectra of 1c under a variety of conditions at room temperature. (d) DSC and TGA (inset) thermograms of the yellow form of 1c upon heating. (e) Variable-temperature emission spectra of the yellow form of 1c upon heating from $-196 \,^{\circ}$ C to 104 $^{\circ}$ C.

The thermotropic properties of the yellow form of **1c** were also investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 2d). TGA study showed that complex **1c** is thermally stable up to 300 °C. The first heating-cooling cycle in DSC thermogram displayed a endothermic signal in the 40–50 °C range, which was ascribed to a structural re-organization of the long alkyl chains of 2,3,4tris(dodecyloxy)benzenesulfonate upon heating. No distinct thermic signals were found in the second heating-cooling cycle, indicating a thermally stable state of **1c** after heating.

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Accordingly, we recorded the variable-temperature emission spectra of the yellow form of **1c** upon heating. Upon temperature varying from –196 °C to 44 °C, the narrow greenish emission band at peak maximum of 549 nm gradually broadened and the intensity continuously decreased. In the 44–64 °C range, the emission jumped abruptly to a peak maximum of 605 nm with much enhanced intensity. Further heating to 104 °C gradually blue-shifted emission to 591 nm and diminished the intensity. The coincidence of the thermograms and variable-temperature emission spectra revealed a pivotal role of the thermal organization of the long alkyl chains of the anions in the close packing of the cations through extensive Pd…Pd interactions.

The typical solvents in which the complexes are soluble are acetonitrile for **1a**, methanol and water for **1b** with a highly hydrophilic anion, and dichloromethane and toluene for **1c** with a highly lipophilic anion. By controlling over the anions, we can study the spectroscopic properties of both individual and aggregated complexes in a variety of solvents including water and toluene with contrasting polarity.



Fig. 3 Absorption and emission spectra of (a) 1a in acetonitrile and (b) 1b in aqueous solutions at a variety of concentrations. Micrographs of these solutions under a 365 nm UV lamp are shown inset.

The diluted acetonitrile solutions of complex 1a at concentrations lower than 4×10^{-4} M were virtually colourless and non-emissive. Upon increasing concentration up to 6.4×10⁻ ³ M, an absorption shoulder at around 420 nm tailing beyond 450 nm emerged and a structureless emission band at peak maximum of 629 nm (Fig. 3a) with a lifetime of 0.16 µs and a quantum yield of 3% was observed. ¹H-NMR signals for the (C^N^N)Pd moiety shifted to the high-field upon concentration increased from 4×10^{-4} to 6.4×10^{-3} M in CD₃CN, while the signals for the NHA moiety remained constant. We inferred dynamic oligomers of 1a with Pd...Pd interactions in concentrated solutions. In comparison, the aqueous solutions of complex 1b at concentrations as low as 1×10⁻⁵ M were emissive (Fig. 3b) at peak maximum of 625 nm (lifetime 0.33 µs, quantum yield 4%). Increasing concentration up to 1×10⁻⁴ M enhanced the 625 nm emission to a quantum yield of 11% and a lifetime of 0.60 $\mu s.$ Absorption tails in the 400–500 nm range were evident in the aqueous solutions of 1b. No accountable ¹H-NMR could be recorded for 1b in D₂O at room temperature even at concentrations as low as 1×10⁻⁵ M, indicating an aggregated state.

The diluted solutions of **1c** in dichloromethane are virtually colourless (only a weak absorption tail beyond 400 nm was recorded) and non-emissive, resembling the diluted acetonitrile solutions of **1a**. Upon gradually decreasing the volumetric

fraction of dichloromethane from 100% to 0 in the dichloromethane/toluene solvent mixtures, the solution appeared red in colour after the volumetric ratio of 3:7 (Fig. 4a) and a distinct absorption band at 528 nm emerged and achieved a molar extinction coefficient of 4300 M⁻¹cm⁻¹ in pure toluene (Fig. 4c). Concomitantly, an orange-red emission (Fig. 4b) at peak maximum of 606 nm emerged (Fig. 4c) and achieved a lifetime of 0.26 µs and a quantum yield of 14% in pure toluene. The excitation spectra monitored at 606 nm gave a distinct lower-energy band at 528 nm, well-matching those found in the absorption spectra. These observations suggested that the cations of 1c exists in a monomeric form in dichloromethane but as oligomeric aggregates in toluene most likely through extensive Pd…Pd interactions. We tentatively assigned the distinct low-energy absorption band at 528 nm to be a metalmetal-to-ligand charge-transfer (MMLCT) transition and the 606 nm phosphorescence to be a ³MMLCT excited state associated with metallophilicity among the Pd(II) NHA cations.

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Fig. 4 Micrographs of **1c** in CH₂Cl₂/toluene solutions with a variety volumetric ratios under ambient light (a) and under a 365 nm UV lamp (b). (c) Absorption and emission spectra of **1c** in CH₂Cl₂/toluene solutions with a variety volumetric ratios at 298 K (concentration ~1×10⁻⁵ M). (d) Variable-temperature absorption and emission (λ_{ex} = 345 nm, isosbestic point) spectra of a toluene solutions of **1c** (concentration ~1×10⁻⁵ M). Inset shows the plot of the fraction of aggregated molecules (α_{agg} , extracted from absorbance at 528 nm) against temperature and the red line is a fitness to the nucleation-elongation model.

The variable-temperature absorption and emission traces of **1c** in toluene were recorded. As shown in Fig. 4d, the distinct low-energy absorptions at 528 nm gradually declined and a peak at 327 nm emerged to give a well-defined isosbestic point at 345 nm upon elevating the temperature from 20 to 80 °C. Accordingly, the 606 nm emission diminished upon temperature increasing, when the excitation wavelength was fixed at 345 nm. Both the absorption at 528 nm and emission at 606 nm can be restored upon decreasing the temperature to 20 °C again, revealing a dynamic and reversible thermal process of **1c** in toluene. At lower temperatures, cations of **1c** exists dominantly in aggregates, which dissociate into monomers at a higher temperature.

A plot of the fraction of aggregated molecules (α_{agg} , extracted from absorbance at 528 nm) against temperature is nonsigmoidal (Fig.4d, inset), and we found that the nucleation-elongation model developed by Meijer, Schenning and Van der Schoot¹⁷ afforded good fits to the variable-temperature absorption changes. Extracted from the data fitness, the nucleation-elongation transition temperature (T_e) was 336.2 K

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(63 °C), the elongation enthalpy (H_e) was -46.9 kJ mol⁻¹, the number-averaged degree of polymerization at T_e ($<N_n(T_e)>$) was 11, and the equilibrium constant of the activation step at the elongation temperature (K_a) is 7.9×10^{-4} M⁻¹. The supramolecular polymerization of complex **1c** in toluene takes place in two phases. Initially, about eleven molecules aggregated into nucleus, and this is an unfavourable nucleation process. After the local concentration of **1c** amounts the critical nucleation, a highly favourable and cooperative growth elongates the aggregates of **1c** into polymers.



Fig. 5 TD-DFT calculated UV-Vis absorption spectra of monomeric and dimeric Pd(II) NHA cation(s) with toluene as solvent. Inset shows the molecular orbitals involved in the lower-energy transitions at the optimized geometry.

We performed time-dependent density functional theory calculations on the monomeric and dimeric structures of the Pd(II) NHA cations in toluene, using B3LYP-D3 functional (B3LYP with dispersion correction) with basis set of 6-31G(d) for C, H, O, and N atoms and LanL2DZ basis set for the Pd atom (see ESI for details). The lowest-energy transition in the calculated absorption spectrum (Fig. 5) of the monomer at 415 nm (oscillation strength 0.003) involves intraligand charge-transfer (ILCT) on the (C^N^N) ligand and Pd(4dz²) to NHA metal-toligand charge transfer (MLCT). In contrast, the calculated lowest-energy transition of the dimeric structure with a close Pd…Pd contact (optimized to be 3.164 Å) is at 489 nm (oscillation strength 0.047), which originates from an electronic transition from the antibonding $d\sigma^*(4dz^2)$ orbital to the weakly stacked (C^N^N) ligand π^* orbital. The calculated and experimental absorption spectra converged to provide compelling evidences for the MMLCT excited state of Pd(II) NHA in aggregated species.

In summary, tridentate cyclometalated Pd(II) allenylidene complexes exhibit highly emissive and sensitive MMLCT excited states in the solid state and as aggregates in solutions. We envisage that the MMLCT photochemistry of Pd(II) could be as rich as that of Pt(II) and that the Pd(II) allenylidene complexes could be strategically harnessed as novel supramolecular synthons for self-assembly reactions.

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Conflicts of interest

There are no conflicts to declare.

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United we shine: Extended intercationic Pd…Pd contacts of 3.30 Å show distinct MMLCT transitions and low-energy emissions.