

Delocalization in Platinum–Alkynyl Systems: A Metal-Bridged Organic Mixed-Valence Compound

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Organometallic “rigid-rod” polymers with π -conjugated metal-organic units are currently receiving much attention because of their potential use as advanced materials for electronic, optical, and liquid crystal applications.¹ Notably, Pt–alkynyl polymers and oligomers have been employed in organic photocells² and have been used as model systems to characterize the triplet manifold of conjugated organic polymers³ relevant to OLED devices.⁴

The performance of electronic devices is influenced to a large extent by the efficiency of intrachain electron and hole migration, or delocalization. However, the question concerning the degree to which Pt disrupts or enhances the π -conjugation between organic units and, hence, alters the electronic structure has still not fully been addressed. Some qualitative insight, in particular concerning the delocalization of the singlet and triplet excitons in Pt–alkynyl species, has been acquired from photophysical studies.⁵ More recently, the π -conjugation has been probed by means of single-molecule charge-transport measurements; it has been found, for instance, that the molecular conductivity of a model Pt-bridged phenylacetylide molecule is significantly higher than that of a π -conjugated oligo(phenyleneethynylene) “molecular wire”,⁶ although it is considerably lower than that of a 9,10-anthracene-bridged analogue.⁷

In this communication, we present a *quantitative* assessment of the effect Pt has on electronic delocalization. We describe a system, **1** (Figure 1), in which two triarylamine redox centers are bridged by Pt; analysis of the intervalence charge-transfer (IVCT) band of its mixed-valence (MV) derivative, **[1]⁺**, allows us to quantify directly the electronic coupling through Pt for the first time and to compare this to that in an all-organic structural analogue previously reported by Lambert,⁸ **[2]⁺** (see Figure 2). Moreover, while inorganic MV systems with both inorganic and organic bridges have been much studied and pure organic MV systems are gaining increasing attention,⁹ **[1]⁺** represents an unusual class of MV system whereby two organic redox centers are coupled through a metal atom.¹⁰

The Pt(II)-bridged triarylamine species, **1**, was synthesized by coupling of *trans*-dichlorobis(triethylphosphine)platinum(II) with (4,4'-dimethoxy,4''-ethynyl)triphenylamine. A single-crystal X-ray diffraction study confirms the *trans* arrangement of ligands across a square-planar Pt center (Figure 1). The electronic absorption spectrum of **1** in CH₂Cl₂ features a strong transition at 373 nm ($\log \epsilon = 4.82$), along with higher energy absorption at 307 nm ($\log \epsilon = 4.60$). The luminescence spectrum shows a weak band at 405 nm assigned to S₁ → S₀ relaxation, along with a much more intense band at 494 nm assigned to the T₁ → S₀ transition. Very similar behavior is observed for Pt–alkynyl polymers,³ and hence **1** may be considered a good model for these systems in terms of

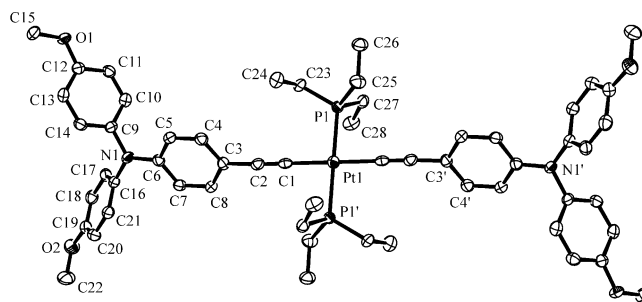


Figure 1. Molecular structure of **1** at 120 K with thermal ellipsoids at 50% probability and all H atoms omitted for clarity. Primed atoms are generated by *C_i* symmetry. Selected distances (Å) and angles (deg): Pt1–Pt1 2.2949(12), Pt1–C1 2.008(5), C1–C2 1.171(7), C2–C3 1.476(7), N1–C6 1.399(6), N1–C9 1.442(6), N1–C16 1.432(6), N1–N1' 17.780(7), C1–Pt1–Pt1 93.07(12), C1–Pt1–P1' 86.93(12), C4–C3–C3'–C8' 3.0(7)

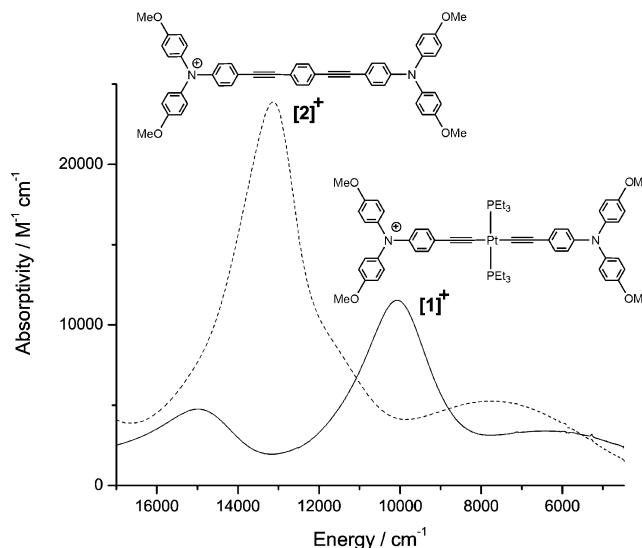


Figure 2. UV-vis-NIR spectra for **[1]⁺** and **[2]⁺** in CH₂Cl₂.

electronic structure and photophysics. Calculations of the excited state of **1** performed at the time-dependent density functional theory (TD-DFT) level reveal that both S₁ and T₁ states originate from orbitals with mixed triarylamine and alkyne character and are, thus, delocalized over the entire system. The energy of 3.4 eV (364 nm) derived for S₁ compares well with the experimental absorption data. TD-DFT calculations also indicate that several more excited states located just above S₁ also contribute to the first absorption band, with energies 3.6–3.7 eV.

Electrochemistry of **1** reveals two overlapping reversible oxidations due to the triarylamine groups, with separation $\Delta E_{1/2} = 65$ mV resolvable by differential pulse voltammetry, indicating the comproportionation constant for the MV monocation, K_C , to be ca.

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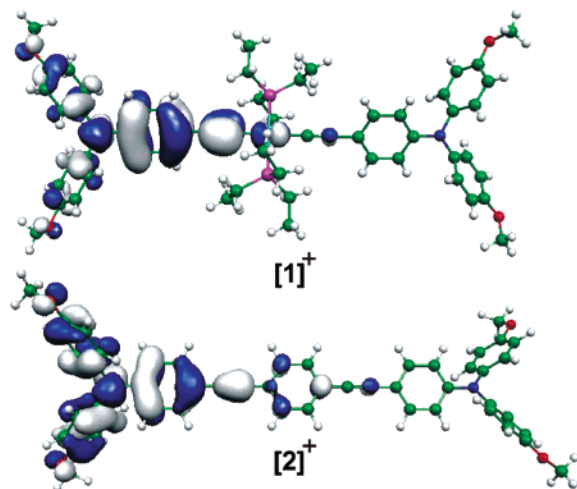


Figure 3. Localized orbitals of $[1]^+$ and $[2]^+$ involved in the ET process.

Table 1. IVCT Band Data for $[1]^+$ and $[2]^+$

cation	$\tilde{\nu}_{\max}$	$\epsilon_{\max}/M^{-1} \text{ cm}^{-1}$	$\Delta\tilde{\nu}_{1/2}$	$R/\text{\AA}$	V/cm^{-1}
$[1]^+$	6540	3395	4200	17.78	350
$[2]^+$	7730	5257	4280	19.30 ^b	440

13 at 298 K.¹¹ Reaction of **1** with 0.1 equiv of tris(4-bromophenyl)-aminium hexafluoroantimonate oxidant in CH_2Cl_2 affords a green solution containing the monocation; the dication is formed by similar reaction of **1** with 2 equiv of oxidant in CH_2Cl_2 . The MV monocation displays a band (6540 cm^{-1}) in the near-IR region of the spectrum attributable to IVCT, along with peaks at 10 000 and $15\,000 \text{ cm}^{-1}$ assigned to $\text{Pt} \rightarrow \text{N}^+$ charge transfer and a localized triarylammonium excitation, respectively. The IVCT band is absent in the electronic spectrum of homovalent $[1]^{2+}$, while the other two transitions are observed at similar energies to $[1]^+$ but with greater intensity; the neutral molecule does not display any features in this region of the spectrum. EPR spectroscopy of $[1]^+$ confirms the first oxidation to be N-based (see Supporting Information). Optical spectra of $[1]^+$ and the benzene-bridged MV monocation $[2]^+$ measured under identical conditions are shown in Figure 2.¹² The IVCT band for $[1]^+$ is of low energy and low intensity; the width at half-height is ca. 4200 cm^{-1} , which is broader than the bandwidth of 3140 cm^{-1} predicted by the Hush model,¹³ suggesting that $[1]^+$ is a Robin–Day Class II system.¹⁴ In the framework of the Hush model, the electronic coupling between nitrogen redox centers, V , may be derived from the following equation:¹³

$$V = 2.06 \times 10^{-2} (\epsilon_{\max} \cdot \tilde{\nu}_{\max} \cdot \Delta\tilde{\nu}_{1/2})^{1/2} / R$$

where R is the donor–acceptor charge-transfer distance in \AA ; for $[1]^+$ this is taken to be the intramolecular N–N crystallographic distance. The derived values of V along with the details of the IVCT bands for $[1]^+$ and $[2]^+$ are listed in Table 1.

Our results reveal that the electronic coupling in the Pt-bridged system is only slightly decreased when compared to that found for the benzene-bridged triarylamine system $[2]^+$. The electronic couplings obtained by using Koopmans' theorem¹⁵ (KT) are nearly twice those derived from IVCT bands but reproduce the same trend. The similarity between the electron-transfer processes in $[1]^+$ and $[2]^+$ is additionally supported by the nature of the active orbitals involved (see Figure 3);¹⁶ both sets of orbitals show very similar delocalization of the triarylamine electron density onto the central bridge.

In summary, we have shown that the electronic coupling through an alkyne–Pt–alkyne bridge is only somewhat smaller than through an alkyne–benzene–alkyne bridge. Thus, we may conclude that electronic delocalization in Pt–alkynyl π -conjugated polymers is not substantially decreased when compared to poly(phenyleneethynylene)s, and hence, the phosphorescent properties imparted to the system by $\text{Pt}^{3,4}$ do not seem to be outweighed significantly by a deleterious reduction in conjugation along the polymer chain.

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Supporting Information Available: Synthetic, computational, and crystallographic details (CIF); electronic spectra, voltammetry, and EPR data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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