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Platinum(II) Diimine Diacetylides: Metallacyclization Enhances Photophysical Properties

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The synthesis, structural characterization, and photoluminescence properties of a new platinum(II) diimine complex bearing the bidentate diacetylide ligand tolan-2,2′-diacetylide (tda), Pt(dbbpy)(tda) [dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine], are described. In CH_2Cl_2, Pt(dbbpy)(tda) exhibits a strong visible charge-transfer absorption and broad emission centered at 562 nm. The photoluminescence quantum yield and excited-state lifetime are 0.52 and 2.56 μs, respectively, at room temperature. These parameters indicate that the planarization and rigidity introduced by the cyclic diacetylide leads to a lower-energy-absorbing species displaying enhanced photophysics relative to the analogous Pt(dbbpy)(C≡CPh)$_2$. Time-dependent density functional theory calculations, which include solvation by CH_2Cl_2 via the polarizable continuum model, are used to reveal the nature of the excited states in these molecules that are responsible for the charge-transfer transitions. The 77 K emission spectra of the two compounds in EtOH/MeOH glasses are compared, uncovering tda-based ligand-localized phosphorescence in the title compound.

The field of platinum(II) charge-transfer chromophores continues to expand as a result of their fundamentally interesting and potentially useful excited-state properties. One exciting class of these square-planar molecules incorporates a single Pt^{II} center, a diimine ligand, and two σ-bonded acetylides.[1−4] These structures possess ground-state metal-to-ligand charge-transfer characteristics that are strongly influenced by acetylide ligand(s) orbital mixing, reminiscent of that observed in Pt(diimine)(dithiolate) complexes.[5] The significant acetylide ligand participation in the ground and excited states of these complexes yields distinct and interesting photophysical behavior. Parallel to recent developments in these charge-transfer systems, Pt^{II}-containing conjugated metallacycles are emerging as a new class of structurally and electronically appealing metal−organic materials.[6−9] Although numerous metallacyclynes have been produced by a variety of research groups, no Pt^{II} molecules have been prepared that combine diimine and diacetylide frameworks within the same structure. This structural motif would preserve the charge-transfer character and restrict the diacetylide ligand geometry to the same plane as the diimine ligand. The imposed rigidity should aid in reducing nonradiative decay and improving electron delocalization in the diacetylide moiety. These features would undoubtedly influence charge-transfer processes that are intimately coupled to the electronic structure within the metallacycle. There is also the possibility for accessing metallacyclyne-localized triplet states using visible light in such molecules. Herein we describe the synthesis, characterization, electrochemistry, and photophysical properties of a prototype platinum(II) diimine diacetylide complex Pt(dbbpy)(tda) (**1**; dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, tda = tolan-2,2′-diacetylide). Compound **1** does indeed exhibit ground- and excited-state properties influenced by the conjugated cyclic diacetylide, as indicated by a direct experimental comparison to Pt(dbbpy)(C≡CPh)$_2$ (**2**).

Compound **1** was prepared by the reaction of Pt(dbbpy)Cl$_2$ with 2,2′-diethynyltolan[6b] in the presence of freshly distilled *i*Pr$_2$NH and a catalytic amount of CuI in dry

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(1) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447−457.

(2) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053−4062.

(3) Chan, S.-C.; Chan, M. C. W.; Wang, Y.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *Chem.*−*Eur. J.* **2001**, *7*, 4180−4190.

(4) (a) Pomestchenko, I. E.; Luman, C. R.; Hissler, M.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2003**, *42*, 1394−1396. (b) Pomestchenko, I. E.; Castellano, F. N. *J. Phys. Chem. A* **2004**, *108*, 3485−3492. (c) Hua, F.; Kinayyigit, S.; Cable, J. R.; Castellano, F. N. *Inorg. Chem.* **2005**, *44*, 471−473. (d) Danilov, E. O.; Pomestchenko, I. E.; Kinayyigit, S.; Gentilli, P. L.; Hissler, M.; Ziessel, R.; Castellano, F. N. *J. Phys. Chem. A* **2005**, *109*, 2465−2471.

(5) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949−1960.

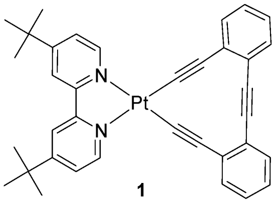
(6) (a) Bradshaw, J. D.; Guo, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2582−2584. (b) Guo, L.; Bradshaw, J. D.; McConville, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, *16*, 1685−1692. (c) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153−3180.

(7) (a) Pak, J. J.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **1997**, *16*, 4505−4507. (b) Johnson, C. A.; Haley, M. M.; Rather, W.; Han, F.; Weakley, T. J. R. *Organometallics* **2005**, *24*, 1161−1172.

(8) Bosch, E.; Barnes, C. L. *Organometallics* **2000**, *19*, 5522−5524.

(9) Campbell, K.; McDonald, R.; Ferguson, M. J.; Tykwinski, R. R. *Organometallics* **2003**, *22*, 1353−1355.

10.1021/ic060102b CCC: $33.50



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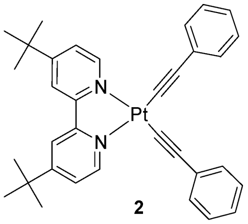

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dichloromethane (CH_2Cl_2). Final purification was achieved by column chromatography on alumina using 4:1 CH_2Cl_2/CH_3CN (acetonitrile). The air-stable, yellow solid was structurally characterized by ^1H and ^{13}C NMR, mass spectrometry, elemental analysis, and Fourier transform IR. Compound **2** was available from our previous studies,[4] and both complexes are soluble in a variety of organic solvents including toluene, CH_2Cl_2, and CH_3CN.

The ground-state absorption spectra of compounds **1** and **2** in CH_2Cl_2 are displayed in Figure 1. There is a dramatic red shift of the charge-transfer absorption in **1** relative to **2**, 427 nm vs 397 nm, respectively. There is also a modest increase in the extinction coefficient in **1** (~5300 M^{-1} cm^{-1}), indicative of improved electronic coupling between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In both instances, these complexes exhibit negative solvatochromic behavior in their lowest-energy absorption bands (see the Supporting Information, SI), likely a consequence of their opposing ground- and excited-state dipole moments.[10] The strong mixing of the tda electron density with the Pt^{II} center in **1** promotes multiple electronic effects manifested in the position and intensity of the lowest-energy transition. Compound **1** illustrates that the incorporation of a conjugated cyclic diacetylide yields a charge-transfer complex red-shifted from the analogous model chromophore **2**. The electronically excited states of **1** and **2** were investigated using time-dependent density functional theory (TD-DFT; see the SI for details). Effects of solvation in CH_2Cl_2 were included via the polarizable continuum model (PCM). The results of these calculations are displayed as vertical bars in Figure 1, with the height of each bar corresponding to the calculated oscillator strength for the transition at that particular wavelength. Virtually all of the electronic transition energies in **1** and **2** were calculated to blue-shift by at least 0.7 eV when solvation effects were included, and to best reproduce the experimental absorption spectra in CH_2Cl_2, we found it necessary to further blue-shift the calculated PCM TD-DFT transition energies by 0.52 eV. These calculations reveal that the lowest-energy absorption band in both compounds arises from two unresolved electronic transitions. In both cases, the low-energy transition is primarily HOMO to LUMO in nature and the higher-energy transition is HOMO-1 to LUMO. The LUMO in both molecules corresponds to the same bipyridine π^* orbital. The HOMO and HOMO-1 involve contributions from both the diacetylide π orbitals and the Pt d orbitals. However, the HOMO in **1** correlates to the HOMO-1 in **2**, and the HOMO-1 in **1** correlates to the HOMO in **2**. In both molecules, the most intense transition (HOMO → LUMO in **1** and HOMO-1 → LUMO in **2)** is associated with the same set of orbitals; a symmetric combination of π orbitals on the two phenyl rings mixed with a Pt d orbital and a bipyridine π^* orbital. This produces a transition dipole moment along the 2-fold rotation axis and therefore antiparallel to the large ground-state dipole moment calculated to be 12.1 D for **1** and 11.7 D for **2**.

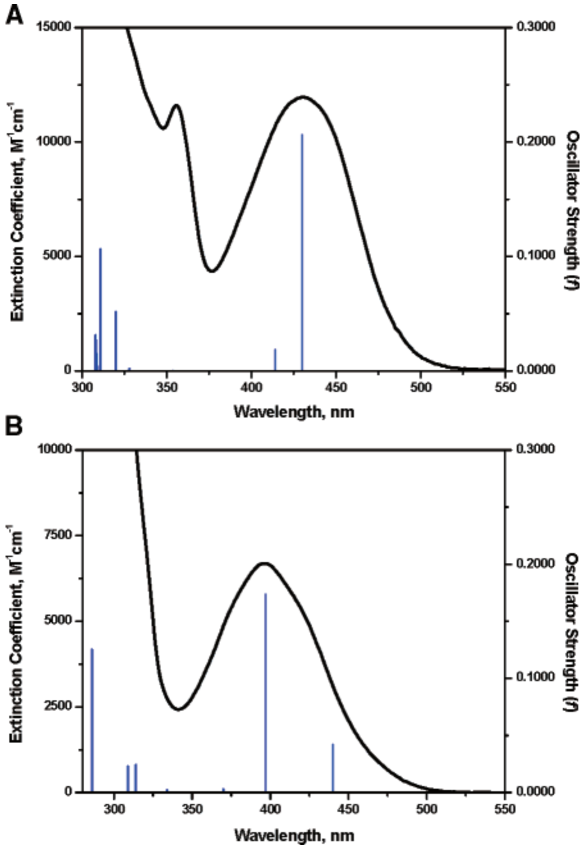

Figure 1. Absorption spectra (black solid lines) and simulated excitation energies (offset by 0.52 eV; see the text) and oscillator strengths (blue vertical lines) calculated by TD-DFT of compounds **1** (A) and **2** (B) in CH_2Cl_2.

Cyclic voltammetry data were obtained in CH_2Cl_2 using a Pt working electrode, referenced to the internal ferrocene (Fc) standard. Complexes **1** and **2** both exhibit one irreversible oxidation, assigned as a HOMO-centered process [metal and acetylide ligand(s)], and the first reduction (reversible) occurs on the dbbpy ligand. The peak anodic currents occur at +0.91 and +0.92 V vs Fc^+/Fc^0 for compounds **1** and **2**, respectively. The dbbpy ligand-based reversible reduction is seen at −1.77 V for **1** and at −1.83 V vs Fc^+/Fc^0 for **2**. Although there are clear differences in the absorption properties between **1** and **2**, the static room-temperature emission spectra are virtually identical with $\lambda_{max} = 562 \pm 2$ nm ($\Phi_{em} = 0.52 \pm 0.05$) and 560 ± 2 nm ($\Phi_{em} = 0.34 \pm 0.05$), respectively (Figure 2). The coincident photoluminescence spectra are broad and structureless, as is typically observed in square-planar platinum(II) diimine acetylide complexes.[1−4] Both of the emission intensity decay transients adequately fit single-exponential functions at room temperature. The excited-state lifetime of **1** measured by transient

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[10] (a) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, The Netherlands, 1984; pp 208−212. (b) Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 499−503.

Table 1. Photophysical and Electrochemical Properties in CH_2Cl_2 at Room Temperature

compd	λ_{abs},[a] nm (ϵ, M^{-1} cm^{-1})	λ_{em},[a] nm	τ_{em},[b] μs	Φ_{em}[b]	k_r,[c] s^{-1}	k_{nr},[d] s^{-1}	ΔG_{ES},[e] eV	$E^{red}_{1/2}$,[f] V	Pt^{II}*/Pt^I,[g] eV
1	427 (12 000)	562	2.56	0.52	2.0×10^5	1.9×10^5	2.49	−1.77	0.72
2	397 (6700)	560	1.36	0.34	2.5×10^5	4.8×10^5	2.54	−1.83	0.71

[a] Absorption and emission maxima, ±2 nm. [b] Photoluminescence quantum yields and intensity decays, ±5%. [c] $k_r = \Phi/\tau$. [d] $k_{nr} = (1 - \Phi)/\tau$. [e] Excited-state energies (ΔG_{ES}) were estimated (±5%) by drawing a tangent on the high-energy side of the emission band. [f] The first reduction potential measured in 0.15 M TBAP/CH_2Cl_2 vs Fc^+/Fc^0, ± 20 mV. [g] Calculated excited-state reduction potentials (vs Fc^+/Fc^0), (Pt^{II*}/Pt^I) = (Pt^{II}/Pt^I) + ΔG_{ES}.

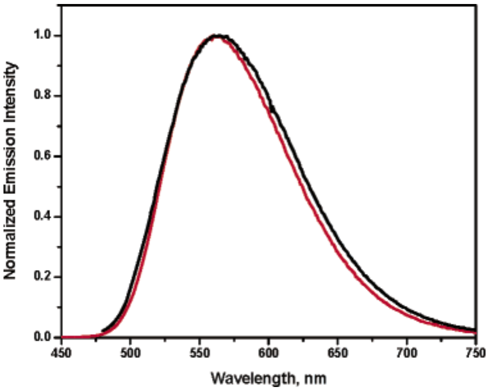

Figure 2. Static emission spectra of compounds **1** (black) and **2** (red) measured in CH_2Cl_2 at 298 K (λ_{ex} = 430 ± 2 nm).

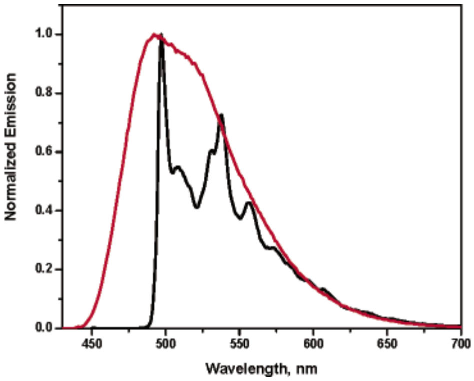

Figure 3. Emission spectra of compounds **1** (black) and **2** (red) measured in 4:1 EtOH/MeOH glasses at 77 K (λ_{ex} = 430 ± 2 nm).

luminescence was determined to be 2.56 ± 0.10 μs in argon-saturated CH_2Cl_2, whereas the complementary experiment performed on **2** yielded a lifetime of 1.36 ± 0.10 μs. The excited-state lifetime and luminescence quantum yield in **1** are enhanced relative to **2,** consistent with the 2.5-fold reduction in the nonradiative rate constant (k_{nr}) calculated for **1**. The improvement in the photophysical properties must have origins in the structural differences between the chromophores because they are practically identical from an energetic standpoint. Work is in progress to understand the origin of the emitting states in these molecules. Complete absorption/emission and electrochemical properties of **1** and **2** are collected in Table 1 along with calculated values of k_r, k_{nr}, and excited-state reduction potentials.

Figure 3 presents the 77 K emission spectra of **1** and **2** measured in 4:1 EtOH/MeOH glasses. The spectrum of compound **2** is identical with that previously reported in the literature under the same conditions as those assigned to the charge-transfer excited state.[2,4b] The band shape and profile of **1** is markedly distinct from those observed in **2**, suggesting a different excited-state parentage at 77 K.[4a] The three sharp peaks seen in the emission spectrum of **1** at 77 K occur at the following energies: 20 121, 18 622, and 17 953 cm^{-1}. Subtraction of the two lower-energy vibrational spacings from the origin peak yields 1499 and 2167 cm^{-1}, respectively. These are attributed to symmetric vibrations localized on the tda moiety; 1499 cm^{-1} is assigned to aromatic ring modes and 2167 cm^{-1} is assigned to an acetylide C≡C mode. DFT calculations performed on **1** in vacuum predict two symmetric C≡C vibrations of small intensity at 2126 and 2200 cm^{-1}. One of these bands is likely responsible for the feature observed in the low-temperature emission spectrum of **1**. The lifetime of **2** at 77 K is 3.51 μs, which is well modeled by a single-exponential function.[4b] In the case of **1**, the 77 K lifetime is complex, adequately modeled by a sum of two single-exponential functions ($\tau_1 = 9.0 \pm 0.3$ μs; $\tau_2 = 20 \pm 0.3$ μs). Both components are significantly longer-lived than the lifetime of compound **2**. The low-temperature photophysics are consistent with an emitting state that is triplet tda in character, meaning that the lowest excited state crosses over from charge transfer to ligand-localized upon cooling from room temperature to 77 K. This is consistent with the notion that charge-transfer excited-state energies increase in low-temperature glasses whereas triplet states associated with various ligands remain fixed in energy.[4b,11]

In summary, we report the synthesis, photophysics, electrochemistry, and electronic structure calculations of compound **1**, which represents a new class of Pt^{II} charge-transfer chromophores bearing a cyclic diacetylide ligand. Our results demonstrate that the metallacyclyne structural motif yields enhanced and red-shifted absorption in addition to improved photophysical properties. TD-DFT calculations reveal the molecular orbitals responsible for the low-energy absorption transitions, substantiating the charge-transfer assignment. At low temperature, the excited states of **1** become localized on the tda ligand, and because of the presence of the internal heavy atom, ligand-localized phosphorescence is observed. These results suggest, that with the proper selection of cyclyne, it may be possible to observe room-temperature triplet state photophysics confined to the diacetylide subunit in related structures.

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Supporting Information Available: Synthesis, experimental details, solvatochromism data, and DFT/TD-DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231−238.