

Coarse and Fine Tuning of the Electronic Energies of Triimineplatinum(II) Square-Planar Complexes

Wei-Hsuan Chen,[†] Eric W. Reinheimer,[‡] Kim R. Dunbar,^{*‡} and Mohammad A. Omary^{*†}*Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203, and Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842*

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[Pt(tbtrpy)X]Y complexes (tbtrpy = 4,4',4''-tBu₃-2,2';6',2''-terpyridine) exhibit charge-transfer absorption bands that can be drastically red-shifted to long-wavelength visible absorptions with arylthiolates as X. Further extension to the near-IR (NIR) region is achieved with 7,7,8,8-tetracyanoquinodimethane (TCNQ⁻) as Y⁻, resulting in black absorbers with continuous UV–vis–NIR absorptions and opening up potential applications in energy research.

The [Pt(triimine)X]Y class of compound has been receiving considerable attention because of its significance in fundamental research in inorganic spectroscopy^{1–4} as well as biochemical applications in DNA intercalation and protein probing,⁵ especially given the open coordination sites in the square plane and the potential water solubility of these ionic species. The rich spectroscopic behavior of this class was discovered by the pioneering work of McMillin et al., who showed that [Pt(trpy)X]⁺ complexes with X⁻ = Cl⁻, NCS⁻, OMe⁻, or OH⁻ possess near-UV and short-wavelength visible absorptions assigned to spin-allowed metal-to-ligand charge-transfer (¹MLCT) transitions, while the emission was attributed to analogous spin-forbidden transitions (³MLCT).¹ Further work, using substituted trpy and other triimines as well as other X and Y groups, has demonstrated an elegant photophysical and electrochemical behavior for members of this class.^{1–4} The remarkable luminescence properties of

these compounds are probably facilitated by the high energy of the charge-transfer absorptions, allowing phosphorescence to occur in the visible region as sensitized by the Pt center. Our interest in these compounds stems from the expansion of the range of their applications to solar energy conversion, electrical conductivity, and molecular magnetism, in addition to our fundamental interests in donor–acceptor chemistry and supramolecular assemblies. We recently reported that neutral (diimine)(dithiolato)platinum(II) and -palladium(II) donor complexes form supramolecular stacks with neutral nitrile acceptors, resulting in adducts with partial charge delocalization, which imparts interesting magneto-optoelectronic properties.⁶ These neutral stacks exhibit favorable properties for solar cell applications, including strong absorptions across a wide spectral range, enhanced extinction coefficients relative to dissociated molecules, and the ability to adsorb to the surface of TiO₂ through the nitrile moieties without requiring conventional anchoring groups such as carboxylates. Poor conversion efficiencies were obtained, however, because the first reduction potential of the nitrile is at a lower energy than the conduction band of TiO₂, thus preventing charge injection.⁶ One of the strategies to circumvent this electrochemical mismatch is to use the anionic form of the organic acceptor as a counterion for the cationic complexes [Pt(tbtrpy)X]⁺ while ultimately targeting solar cells based on SnO₂,⁷ whose conduction band lies at lower energy than the reduction potential of the stable nitrile radical anions. In analogy to similar inorganic–organic hybrid materials, the [Pt(tbtrpy)X]⁺TCNQ⁻ adducts might also exhibit interesting conducting⁸ and magnetic⁹ applications. This Communication represents our first contribution in this ongoing expansion, in which we report the syntheses,

* To whom correspondence should be addressed. E-mail: omary@unt.edu (M.A.O.), dunbar@mail.chem.tamu.edu (K.R.D.).

[†] University of North Texas.

[‡] Texas A&M University.

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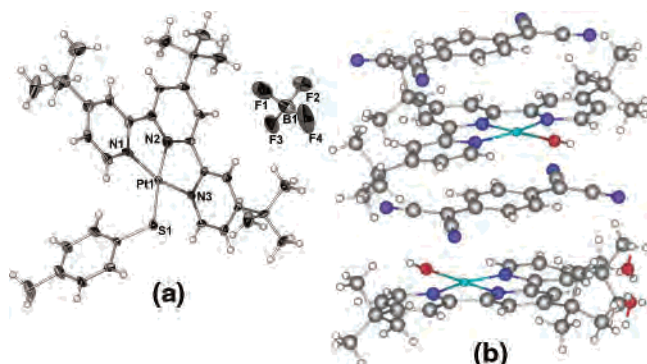
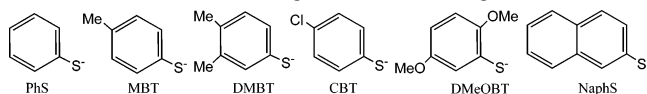


Figure 1. (a) Molecular structure of [Pt(tbtrpy)(MBT)]BF₄ (50% e-lipsoids). Crystal data: orthorhombic, *Pca*2₁, R1 = 0.0427, *a* = 20.91(9) Å, *b* = 19.83(8) Å, *c* = 15.93(13) Å, *Z* = 4. Coordination geometry: Pt–N 2.018(7), 1.949(11), and 2.036(8) Å, Pt–S 2.306(3) Å, N1–Pt–N2 80.5(4)°, N2–Pt–N3 80.6(4)°, N1–Pt–S1 102.2(3)°, and N1–Pt–S1 96.8(2)°. (b) A portion of the stacking arrangement of cations and anions in [Pt(tbtrpy)(OH)]TCNQ. Crystal data: orthorhombic, *Pbcn*, R1 = 0.1008, *a* = 13.84(3) Å, *b* = 23.17(4) Å, *c* = 23.38(4) Å, *Z* = 8. Coordination geometry: Pt–N 1.957(20) Å, Pt–O 2.236(12) Å, N1–Pt–N2 81.1(5)°, N2–Pt–N3 80.8(5)°, N1–Pt–O1 100.4(5)°, and N3–Pt–O1 97.7(5)°. Interplanar separation between centroids: 3.502 Å.

Chart 1. Structures of ArS[−] Ligands and Their Designations



crystal structures, absorption, and electrochemical properties of several [Pt(tbtrpy)X]Y complexes and we demonstrate that a systematic variation of X and Y results in coarse and fine tuning of the electronic energies.

The synthesis involves reactions of [Pt(tbtrpy)Cl]Cl with an equimolar amount of X[−] (NCS[−], OH[−], or various ArS[−] shown in Chart 1) followed by metathesis of the counterion. The products were characterized by standard analytical techniques; see the Supporting Information (SI). The X-ray structures for two representative products are shown in Figure 1; crystallographic details are provided in the SI. Both cations exhibit distorted square-planar coordination (angle ranges are 80.5–102.2° and 80.8–100.4°, respectively). The bond distances and angles within the Pt^{II} coordination sphere are similar to those found for analogous square-planar complexes. The 1:1 stacking motif between [Pt(tbtrpy)(OH)]⁺ and TCNQ[−] shows an interplanar separation of 3.502 Å, within the 3.2–3.6-Å range reported for binary materials of TCNQ and tetrathiafulvalene (TTF).¹⁰ The metrical parameters for the TCNQ unit in [Pt(tbtrpy)(OH)][TCNQ] are in accord with a reduced form of TCNQ and fall in the ranges noted for TCNQ[−] and TCNQ^{2−} (see Table S4, SI).¹¹ Neither compound exhibits Pt···Pt interactions.

Figure 2 shows the electronic absorption spectra for selected compounds, while Table 1 and the SI provide more absorption data for all compounds studied. The high-energy

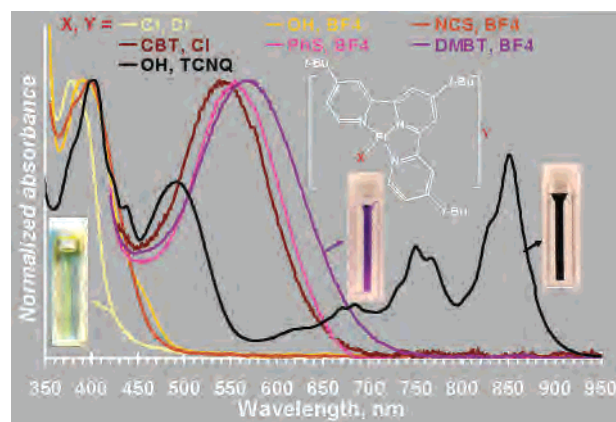


Figure 2. Normalized absorption spectra of selected [Pt(tbtrpy)X]Y complexes in dichloromethane solutions at ambient temperature.

Table 1. Absorption Data for [Pt(tbtrpy)X]Y Complexes in Dichloromethane Solutions at Ambient Temperature

X, Y	λ_{\max}/nm ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)
Cl, Cl	225 (45), 256 (49), 281 (43), 304.5 (24), 330.5 (18), 345.5 (8.3, sh), 378 (3.9)
NCS, Cl	280.5 (33), 302.5 (18), 330 (12), 378.5 (2.8), 392.5 (2.6)
CBT, Cl	281 (27), 313 (13), 329 (12), 344 (12), 377 (25), 538 (1.0)
PhS, Cl	248 (28), 280 (17), 314 (9.5), 542 (0.25)
NaphS, Cl	258 (50), 282 (30), 303 (20), 329 (15), 344 (14), 366 (4.7, sh), 555 (1.3)
MBT, Cl	313 (17), 328 (15), 344 (14), 384 (2.9), 555 (1.6)
DMeOBT, Cl	283 (21), 312 (16), 331 (14), 347 (8.7), 377 (3.1), 562 (0.48)
DMBT, Cl	314 (15), 328 (14), 345 (12), 381 (3.0, sh), 562 (1.6)
OH, BF ₄	261 (26), 281 (21), 312 (12), 334 (10), 391 (2.1)
NCS, BF ₄	246 (34), 280 (23), 305 (13), 315.5 (12), 331 (12), 399 (2.9)
CBT, BF ₄	255 (32), 314 (13), 328 (11), 344 (11), 550 (1.3)
PhS, BF ₄	259 (30), 286 (21), 314 (12), 331 (12), 344 (8.0), 380 (2.2), 555 (0.71)
MBT, BF ₄	261 (44), 314 (16), 327 (15), 344 (13), 382 (3.0, sh), 563 (1.7)
NaphS, BF ₄	255 (42), 303 (16), 329 (12), 343 (10), 382 (29), 564 (11)
DMeOBT, BF ₄	253 (39), 282 (24), 313 (20), 343 (12), 378 (3.4), 563 (1.2)
DMBT, BF ₄	257 (58), 313 (22), 329 (21), 344 (15), 383 (4.5, sh), 571 (1.8)
OH, TCNQ	251 (35), 278 (27, sh), 312 (15), 328 (14), 341 (16), 405 (14), 440 (7.3), 491 (8.7), 686 (2.6), 750 (5.5), 766 (5.0), 851 (10)
NCS, TCNQ	245 (63), 306.5 (23), 316.5 (23), 333 (28), 400 (68), 487.5 (4.0), 683 (7.1), 689 (6.8), 748 (19), 764 (18), 848.5 (36)
PhS, TCNQ	249.5 (21), 316.5 (7.5), 333 (8.5), 405.5 (11), 422.5 (8.9, sh), 490 (0.72), 686.5 (2.7), 749.5 (7.7), 767 (6.9), 851.5 (14)
MBT, TCNQ	251 (41), 313 (16), 327 (15), 341 (15), 407 (17), 421 (16), 492 (7.0), 685 (5.2), 749 (13), 766 (12), 850 (25)
DMBT, TCNQ	259 (43), 313 (16), 330 (16), 410 (18), 422 (19), 494 (3.1), 686 (6.0), 750 (17), 767 (15), 851 (31)

region at $\lambda < 350$ nm (not shown in Figure 2) is dominated by π – π^* transitions localized on trpy, which are generally insensitive to X and Y. The longer-wavelength regions represent transitions due to charge transfer (CT) to the triimine as well as TCNQ-localized transitions in the binary materials. The CT bands are ¹MLCT transitions with X = Cl, NCS, or OH, following McMillin et al.'s assignment,¹ while changing X to ArS leads to a drastic red shift to the visible region. In the [Pt(tbtrpy)ArS]⁺ series, electron-donating and -withdrawing substituents red- and blue-shift the CT absorptions, respectively. These trends are reminiscent of those obtained for the Pt(diimine)X₂ complexes upon changing the anionic X ligands from halides or pseudohalides to various dithiolates.¹² Hence, we assign the visible absorp-

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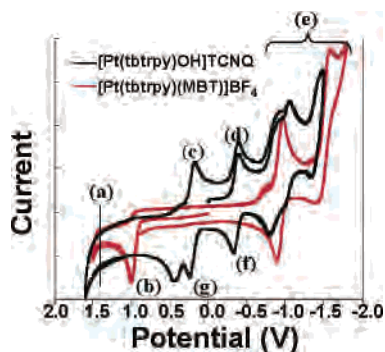


Figure 3. Cyclic voltammograms for two representative compounds in dry CH_2Cl_2 . Peak assignment: (a) free thiolate oxidation; (b) coordinated thiolate oxidation; (c and g) $\text{TCNQ}^0 \leftrightarrow \text{TCNQ}^-$; (d and f) $\text{TCNQ}^- \leftrightarrow \text{TCNQ}^{2-}$; (e) coordinated tbtrpy reduction. Free tbtrpy reduction occurs at potentials more negative than -2.0 V in THF (insoluble in CH_2Cl_2).

tions in $[\text{Pt}(\text{tbtrpy})\text{ArS}]^+$ to CT transitions from mixed thiolate/Pt π -filled orbitals to trpy π^* -vacant orbitals. We prefer this assignment to the interligand CT assignment proposed for similar complexes in which the S-donor ligands included heterocyclic or macrocyclic moieties¹³ because of the analogy with the aforementioned (diimine)(dithiolate) analogues and because a previous study by Che et al.^{13b} and preliminary data herein (Figure S2, SI) suggest a blue shift on changing the metal from Pt^{II} to Pd^{II} . A solvatochromic effect is expected with such an assignment, which we have confirmed (e.g., λ_{max} shifts from 563 to 532 nm for $[\text{Pt}(\text{tbtrpy})\text{MBT}]\text{BF}_4$ on changing the solvent from CH_2Cl_2 to acetonitrile). We also observe a consistent red shift and an increased molar absorptivity for the CT bands with a change in counterion from $\text{Y}^- = \text{Cl}^-$ to $[\text{BF}_4]^-$ (Table 1). The blue-shifted CT bands with $\text{Y} = \text{Cl}$ can be attributed to the stabilization of the polar ground state of $[\text{Pt}(\text{tbtrpy})\text{ArS}]^+$ by the stronger electrostatic interaction with Cl^- as compared to $[\text{BF}_4]^-$.

Further coarse tuning of the electronic absorption energies of $[\text{Pt}(\text{tbtrpy})\text{X}]\text{Y}$ into the NIR region is achieved by changing Y^- from the “spectroscopically innocent” counterions Cl^- and $[\text{BF}_4]^-$ to the stable organic radical TCNQ^- . The structured absorptions in the 600–900-nm range shown in Figure 2 for $[\text{Pt}(\text{tbtrpy})\text{OH}]\text{TCNQ}$, also exhibited by all $[\text{Pt}(\text{tbtrpy})\text{X}]\text{TCNQ}$ salts, are attributed to essentially unperturbed transitions localized on TCNQ^- .¹⁴ Interestingly, $[\text{Pt}(\text{tbtrpy})\text{X}]\text{TCNQ}$ salts also exhibit an absorption peak near 490 nm (Figure 2), in the region of the major absorption band of the TCNQ^{2-} dianion.¹⁴ We hypothesize a charge delocalization in the binary salts by which the cation is partially oxidized to $[\text{Pt}(\text{tbtrpy})\text{X}]^{(1+\delta)+}$ while the anion is partially reduced to $\text{TCNQ}^{(1+\delta)-}$. Consistent with this hypothesis are the IR $\nu_{\text{C}=\text{N}}$ frequencies in $[\text{Pt}(\text{tbtrpy})\text{X}]\text{TCNQ}$ salts (e.g., 2180 and 2178 cm^{-1} with $\text{X} = \text{PhS}$ and DMBT, respectively), clearly red-shifted from those for LiTCNQ (2195 cm^{-1}) or TTF/TCNQ salts, which exhibit intermediate

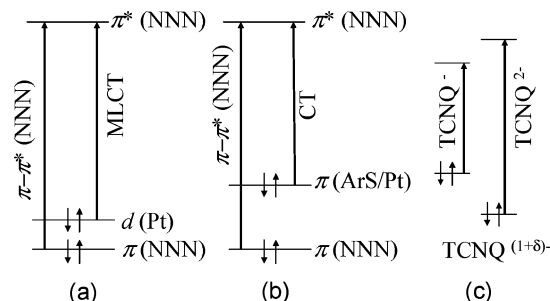


Figure 4. Qualitative assignment of transition types in $[\text{Pt}(\text{NNN})\text{X}]\text{Y}$ complexes with (a) $\text{X} = \text{Cl}, \text{NCS},$ or OR , (b) $\text{X} = \text{ArS}$, and (c) additional bands when $\text{Y} = \text{TCNQ}$. NNN represents the terpyridine moiety.

values between those for neutral TCNQ (2227 cm^{-1}) and TCNQ^- .¹⁵ Partial reduction of TCNQ species is known to lead to absorption signatures of the fully reduced species, as found in the literature of TTF/TCNQ binary organic species¹⁶ and as we⁶ and others¹⁷ reported for inorganic–organic donor–acceptor adducts. Partial reduction attains smaller ϵ values than those in fully reduced species. We note, however, that the available crystallographic data do not always correlate with the corresponding spectral data for TCNQ species in general (Table S4, SI). Further theoretical and crystallographic studies are warranted to assess the aforementioned hypothesis.

The electrochemical data in Figure 3 and the SI further support the electronic structure that we propose in Figure 4. All complexes exhibit trimine-based reversible reductions, consistent with the proposed lowest unoccupied molecular orbital. Complexes with arylthiolates exhibit irreversible oxidations absent with other X groups, in accord with the proposed highest occupied molecular orbital. The compiled data here and in refs 1–4 reinforce the assignment proposed in Figure 4a,b for $[\text{Pt}(\text{tbtrpy})\text{X}]^+$. Compounds with $\text{Y}^- = \text{TCNQ}^-$ exhibit additional redox couples characteristic of this counterion. The communication with the Pt^{II} center shifts the potentials of the trpy-, ArS-, and TCNQ -based redox processes.

Work is underway to assess the suitability of $[\text{Pt}(\text{tbtrpy})\text{X}]\text{Y}$ species for dye-sensitized solar cells and molecule-based magnetic and conducting materials.

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Supporting Information Available: A CIF file for the two X-ray structures and a PDF file providing further experimental details and data for all compounds studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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