Altering Molecular Photophysics by Merging Organic and Inorganic Chromophores

Published as part of the Accounts of Chemical Research special issue "Ultrafast Excited-State Processes in Inorganic Systems".

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CONSPECTUS: Photofunctional molecules and assemblies lie at the heart of many important fundamental processes in nature, and researchers have generated multitudes of artificial chromophores intended to mimic these naturally occurring systems. As dynamic spectroscopic techniques are becoming more widely available, ultrafast techniques in particular, substantial insight continues to be gleaned from the initial photon stimulation event through internal conversion, structural rearrangements, intersystem crossing, energy migration, electron transfer events, and ultimately regeneration of the ground state chromophores in both naturally occurring and inspired chromophores.

This Account details research endeavors motivated by the concept that merging organic and inorganic chromophores can lead to new molecules exhibiting novel excited state properties. Moreover, these excited state properties can be fundamentally understood using combinations of static and dynamic spectroscopic tools, yielding systematic improvements to molecules poised for application in diverse research areas including light-harvesting, lifetime engineering, photocatalysis, and photochemical upconversion. Initial explorations focused on utilizing Förster energy transfer processes in Ru^{II}-based metal−organic chromophores for solar light-harvesting while maintaining long excited state lifetimes. This eventually led to molecules exhibiting triplet−triplet energy transfer between energetically proximate triplet states featuring thermally activated photoluminescence from the upper charge transfer excited state with markedly extended lifetimes. Interest in systematically producing long-lived excited states with concomitant large Stokes shifts inspired the development of numerous Pt^{II} bipyridyl and terpyridyl acetylide charge transfer chromophores featuring ultrafast intramolecular energy migration, high quantum yield ligand-localized phosphorescence at room temperature, and synthetically tunable excited state absorption properties. This structural motif also made it possible to access the triplet excited states of perylenediimide chromophores, permitting quantitative examination of internal conversion and intersystem crossing processes in these complex molecules. The generation of new metal−organic structures featuring unique photophysics appears limitless and simply requires the continued ingenuity of researchers.
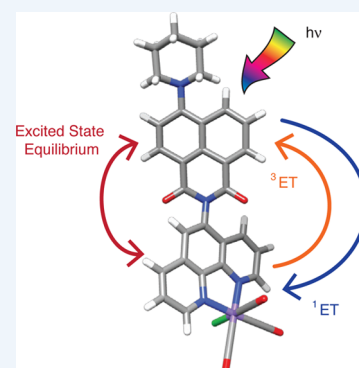
INTRODUCTION

Giacomo Ciamician (1857−1922), a Professor of Chemistry from the University of Bologna considered to be the "Father of Photochemistry", ended his 1912 *Science* paper entitled "The Photochemistry of the Future" with the following question: "Would it not be advantageous to make better use of radiant energy?"[1] Of course he was referring to the almost exclusive use of fossil fuels for the world's energy needs while sunlight was being ignored as a freely available power source. More than 100 years have passed since the publication of this article and unfortunately we still rely on fossil fuels for most of our energy needs. However, the concept of sunlight-driven photoactivation developed by Ciamician and the innumerable scientists that followed led to deep understanding of molecular photochemistry, photophysics, and excited state processes. The sentiment of the question posed above continues to inspire fundamental and applied research problems focused on making better use of solar photons to make and break chemical bonds, which ultimately relies on controlling

molecular excited states. This *Account* details recent progress on the latter accomplished through the hybridization of organic and inorganic components, known as metal−organic chromophores. The metal−organic classification was first coined by Kirk Schanze at the University of Florida to emphasize the importance of the "organic" component(s) without implicating the need for metal−carbon bonds characteristic of organometallics.[2]

The strategic fusion of organic and inorganic subunits into new photofunctional molecules represents a frontier research area that continues to markedly expand, broadly impacting programs engaged in both fundamental and applied processes involving photon stimulation. In particular, the merging of inorganic-based charge transfer complexes with one or more organic chromophores produces new molecular species,
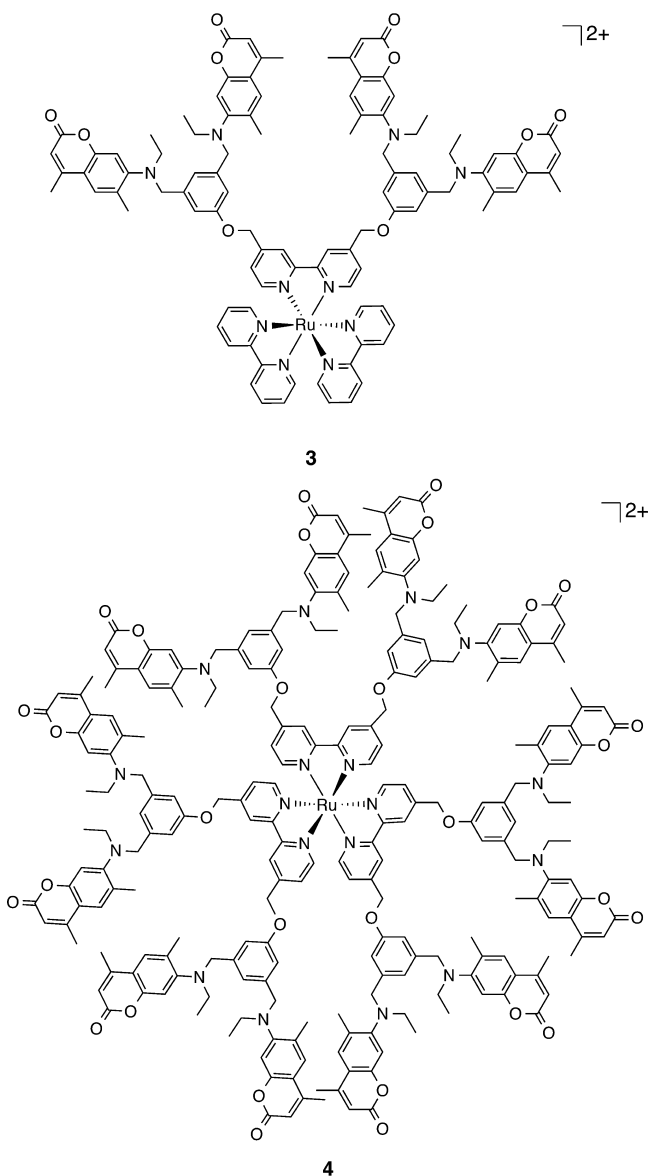
sometimes exhibiting unusual singlet and triplet state photophysics and associated excited state dynamics, but almost universally enables ultrafast excited state energy or electron transfer processes between the components. Depending upon the nature of the chemical linker(s) and requisite energy levels of the components, strong electronic mixing leads to unique photophysical properties from the collection of constituent chromophores and weaker coupling produces architectures exhibiting characteristics reminiscent of the individual molecular subunits. In some instances, excited state equilibrium can be established between the inorganic and organic chromophores resulting in systematically tunable and cooperatively enhanced excited state properties, lifetimes in particular, that can be exploited in a variety of applications. This Account is intended to provide a historical perspective of how our initial research interests in the photochemistry of metal−organic light-harvesting chromophores, singlet/triplet energy transfer processes and excited state engineering, combined with a battery of static and transient spectroscopic tools, conspired to yield a broader understanding of molecular photoprocesses across a number of classes of metal−organic chromophores over the past 16 years.

■ SENSITIZATION OF MLCT EXCITED STATES WITH COUMARIN LASER DYES

In September of 1998, my research group at Bowling Green State University embarked on a series of investigations using coumarin-based laser dyes as UV light-harvesting antennae to sensitize the long-lived metal-to-ligand charge transfer (MLCT) excited states of Ru^{II} polypyridyl complexes. At the time, there was a worldwide effort focused on the synthesis and transient spectroscopic characterization of various artificial light-harvesting arrays constructed from numerous molecular subunits, inspired of course by natural photosynthetic pigments.[3−5] We were specifically interested in molecules that produced long-lived excited states that could potentially activate subsequent bimolecular chemical reactions, serve as extrinsic luminescence probes, or even engage in lifetime-based chemical sensing applications. Fortunately, my first graduate student Dan Tyson, currently employed at DayGlo Corporation in Cleveland, possessed both the drive and synthetic talent necessary for this project to achieve success. The initially investigated Ru^{II} chromophores **1** and **2** displayed long-lifetime and high quantum yield photoluminescence while exhibiting the characteristics of nearly 100% intramolecular energy transfer between the appended coumarin dye(s) and the inorganic core when excited in the UV.[6] Energy transfer was quantified through the magnitude of fluorescence quenching of the coumarin dye(s), the MLCT photoluminescence excitation spectra, and the lack of a rise time in the MLCT-based photoluminescence sensitized through UV excitation in time-correlated single photon counting experiments (∼300 ps time resolution). In order to establish that the mechanism of singlet energy transfer was indeed Förster-type in nature, we evaluated intermolecular energy transfer quenching between coumarin-460 and $[Ru(bpy)_3]^{2+}$ in solution.[7] Lifetime quenching of the coumarin-460 fluorescence on nanosecond time scales by $[Ru(bpy)_3]^{2+}$ in both viscous (glycerol) and fluidic solvents quantitatively fit models for long-range Förster-type transfer, revealing that this was the operative energy transfer mechanism. This represented the first quantitative experimental evidence demonstrating that Förster-type dipole−dipole singlet energy transfer occurs from an excited singlet fluorophore to a MLCT complex in separated chromophores.
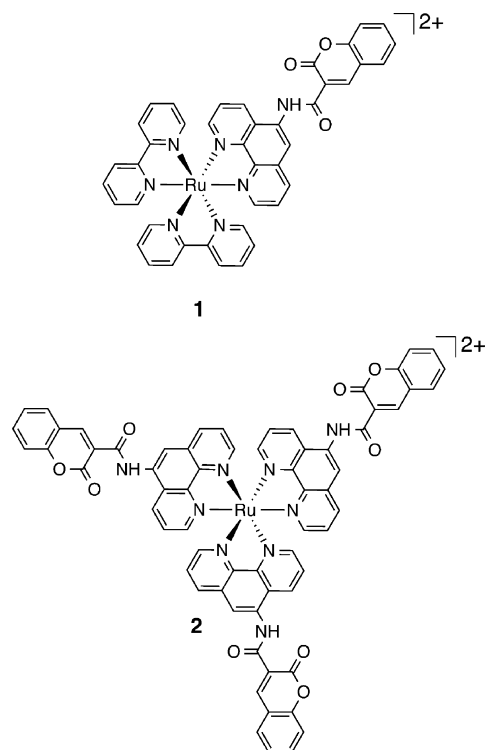
The initial design of one (**1**) or three (**2**) appended coumarins was further expanded by another student at the time, Xiaoli Zhou, who managed to fuse four (**3**) and 12 (**4**) coumarin-450 dyes to a Ru^{II} MLCT core using aryl ether dendritic wedges covalently linked to the 4,4′-positions of 2,2′-bipyridine, generated through a popular divergent synthetic methodology.[8] This ligand motif was inspired by the poly(arylether) dendrimer frameworks developed by Fréchet and co-workers[9] and adapted to Ru^{II} MLCT excited states generating a peripheral-to-core energy gradient as pioneered by the Balzani group in Bologna.[10] Not surprisingly, the coumarin-to-Ru^{II} energy transfer efficiencies in **3** and **4** were nearly quantitative as ascertained by the experiments mentioned above and rendered molecules exhibiting long excited state lifetimes and photoluminescence quantum efficiencies, now slightly insulated from the solvent environment and possessing quite large molar absorptivities centered at 343 nm, impressively 130 000 M^{-1} cm^{-1} in **4**. The latter enabled luminescence detection of femtomolar solutions of this molecule, important for analytical and imaging applications of luminescence spectroscopy. Dan Tyson further examined the photochemistry of **3** and **4** successfully engaging in a number of characteristic bimolecular excited state electron transfer reactions including oxidative and reductive quenching with methyl viologen and phenothiazine, respectively, in addition to triplet−triplet energy transfer with 9-methylanthracene.[11] Unfortunately, oxidative quenching by methyl viologen ultimately led to the cleavage of the ether linkages holding the coumarin-450 dyes in place around the coordination periphery. This was not too surprising given numerous literature examples illustrating the oxidative instability of related linkages.[12] The characteristic $MV^{+•}$ blue-colored radical persisted indefinitely while coumarin-460 fluorescence became easily visualized, indicative of permanent chemical changes to **3** and **4** as a result of the redox-triggered bond cleavage.
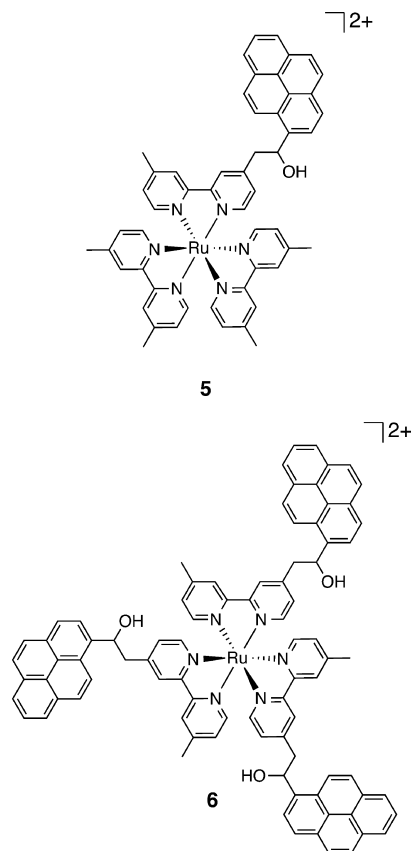
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analog of E-type (eosin-type) thermally activated delayed fluorescence. In E-type delayed fluorescence, excitation into the $S_0 \rightarrow S_1$ transition of eosin leads to high efficiency intersystem crossing to the long-lived T_1 excited state, which thermally repopulates S_1 due to the small S_1-T_1 energy gap, resulting in the observation of delayed fluorescence.[14]

In 1999, thanks again largely to the efforts of Dan Tyson, we published our first manuscript on this subject, describing the photophysical characteristics of the Ru^{II}/pyrenyl molecules **5** and **6**.[15] The initial surprising result was that the excited state

5

6

EXCITED STATE EQUILIBRIA BETWEEN d^6 MLCT COMPLEXES AND ORGANIC CHROMOPHORES

Pyrenyl-Containing Structures

In parallel to the studies above, we were also engaged in combining the light-harvesting singlet transfer processes described above while strategically targeting organic subunits with triplet state energies similar to that of the MLCT chromophore to which they were covalently attached. This would afford new classes of molecules exhibiting large absorption cross sections and long excited state lifetimes valuable for numerous applications as well as the photo-activation of numerous bimolecular reactions in solution. In the 1990s, there was a small body of literature related to the generation of triplet equilibrium between Ru^{II} polypyridyl complexes and a lone pendant pyrene moiety projecting from one of the coordinated ligands; a phenomenon first reported in 1992 by one of my former Bowling Green colleagues Michael A. J. Rodgers.[13] The chromophore topology yields significant excited state lifetime extension in the photoluminescent MLCT excited state, which is populated from the much longer-lived lower-lying pyrene triplet state. This is essentially a triplet state

lifetimes ascertained by transient photoluminescence as well as laser flash photolysis for **5** and **6** were 3 and 9 μs, respectively. These results clearly illustrated for the first time that the number of appended pyrenyl chromophores, one in **5** and three in **6**, had a pronounced influence on the observed excited state lifetimes, which appeared to be linearly proportional to the number density of pyrene triplet acceptors present. Our colleagues in Italy expanded this concept, ultimately demonstrating linear increases in excited state lifetime in related Ru^{II} bipyridyl molecules containing up to six pyrenyl subunits,[16] leaving little doubt about the deterministic nature of this approach to control excited state decay. Other work from our group at the time included the preparation of **7** and **8** and illustrated that minor structural changes to the chromophores proved crucial in controlling the excited state lifetime, which was now well above 100 μs at RT,[17] a conclusion also drawn from the work of Raymond Ziessel and Tony Harriman around the same time.[18] A simple change from an ethyl spacer to a single C–C bond markedly increased the excited state lifetime in these molecules by shifting the equilibrium in favor of the pyrene reservoir. Raymond and I began a collaboration around this time, which has endured to the present day. Some of these early collaborative papers were also aligned with this general
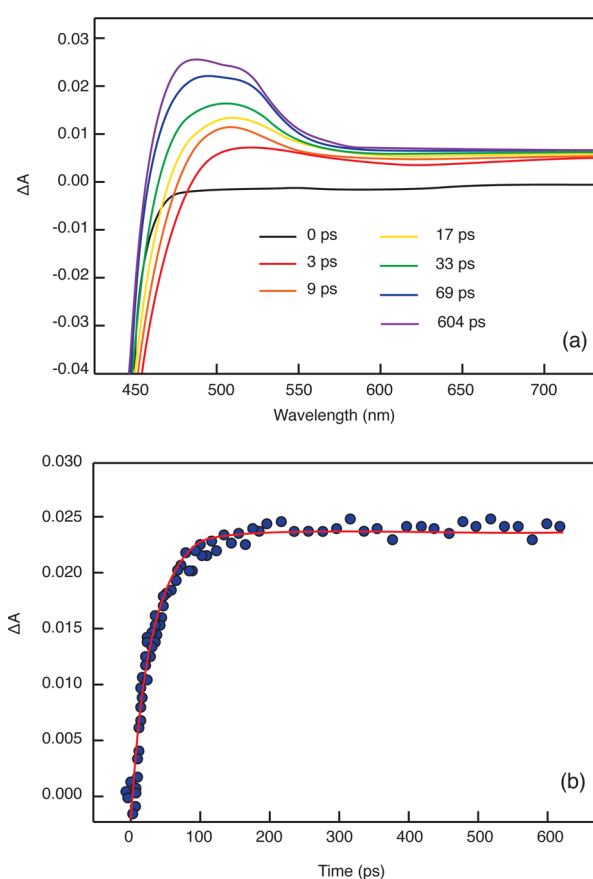
7   **8**

Figure 1. (a) Ultrafast transient differential absorption spectra recorded at various delay times after excitation of **7** with 400 nm pulsed laser excitation. (b) Kinetic profile of the transient at 500 nm fit to a single-exponential model (red line) with a growth rate of 2.8×10^{10} s^{-1} (35.7 ps). Adapted from ref 22.
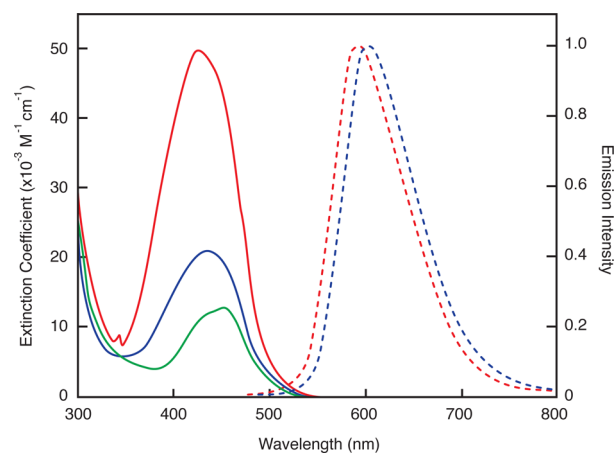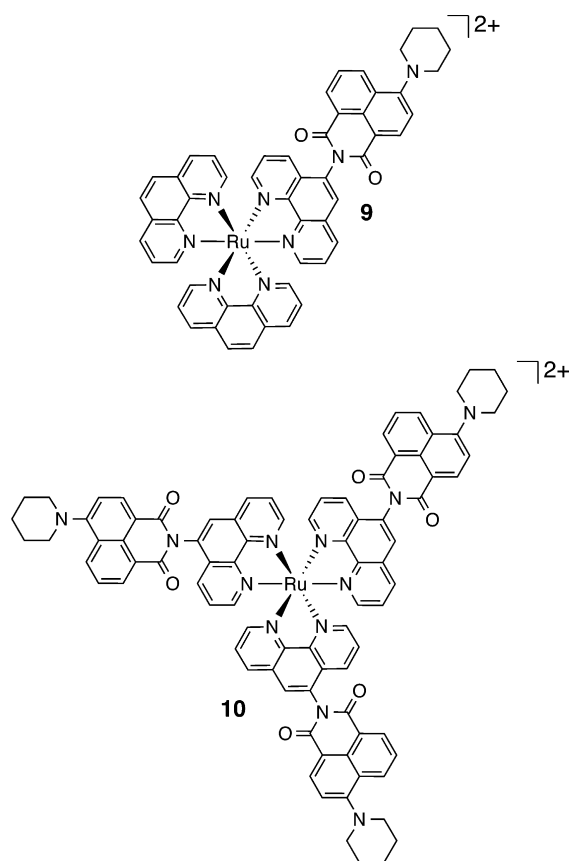
theme of evaluating the unusual photophysical properties of Ru^{II} chromophores bearing multiple pyrenyl auxiliaries,[19−21] albeit strategically positioned and purposely π-conjugated to the coordinating diimine ligands. The availability of ultrafast transient absorption spectroscopy in the laboratory of my former colleague Michael Rodgers permitted the evaluation of the excited state dynamics of **7** and **8**, initiating from ~120 fs after light excitation.[22] Formation of the triplet-to-triplet absorption in pyrene was directly monitored in both complexes and ranged from 2.8×10^{10} s^{-1} in **7** to 2.4×10^{11} s^{-1} in **8**, reflecting the rate differences associated with the number of pyrenyl moieties resident in each structure. The first series of ultrafast data ever recorded during my own independent investigations related to **7** are presented in Figure 1.[22] Although we did not recognize this at the time, the self-quenching processes we reported for **8** in that contribution were likely a result of triplet−triplet annihilation, which would eventually become a focus area of my future research program.[23]

Naphthalimide-Containing Structures

In 2001, we published a paper that was truly a combined effort from everyone in the research group at that time, detailing the unique photophysical properties in naphthalimide containing **9** and **10**,[24] representing the first examples of triplet excited state equilibrium in metal−organic chromophores that did not rely on pyrene reservoirs. These Ru^{II} complexes displayed enhanced absorption properties due to the pendant 4-piperidinyl-1,8-naphthalimide (PNI) chromophore(s), Figure 2. The intense green singlet fluorescence characteristic of the PNI subunit(s) was nearly quantitatively quenched and sensitized the MLCT-based red photoluminescence through Forster-type singlet energy transfer as can be inferred from the data presented in Figure 2. Excitation into either the singlet intraligand (^{1}IL) or ^{1}MLCT absorption bands results in the formation of both ^{3}MLCT and ^{3}IL excited states; each was conveniently monitored by transient absorption and photoluminescence spectroscopy. The relative energy ordering of these triplet states was determined using time-resolved emission spectra at 77 K where dual emission in both Ru^{II} complexes was observed. The shorter-lived higher energy emission had a spectral profile consistent with that typically observed from ^{3}MLCT excited states, whereas the millisecond lifetime lower energy band was attributed to ^{3}IL phosphorescence from the PNI chromophore. At room temperature, the data were consistent with an excited-state equilibrium between the higher energy ^{3}MLCT states and the lower energy ^{3}PNI states. Both complexes displayed MLCT-based emission with room-temperature lifetimes ranging between 16 and 115 μs depending upon solvent and the number of PNI chromophores present. At 77 K, it was

Figure 2. Electronic and uncorrected emission spectra of [Ru(bpy)$_3$]$^{2+}$ (green), **9** (blue), and **10** (red) in CH$_3$CN. Emission spectra of **9** (dashed blue) and **10** (dashed red) were measured at 22 °C using 450 nm excitation. Adapted from ref 24.

apparent that the two triplet states were no longer in thermal equilibrium and independently decayed to the ground state.
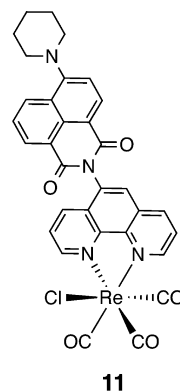
Several years later, we exploited the high oscillator strength infrared C=O bands of **9** and **10** using step-scan FT-IR spectroscopy to support the ^{3}IL excited state assignments through vibrational spectroscopy.[25] Transient infrared spectroscopy

9

10

11

vibrations of magnitude similar to those measured experimentally. These results illustrated that triplet electron density can be directly tracked through time-resolved infrared measurements in metal−organic chromophores and that frequency shifts comparable to those observed in charge-transfer systems can be realized.

In 2011, we fortunately possessed the experimental infrastructure at BGSU necessary for the complete dynamic photophysical characterization of the Re[I] carbonyl complex **11** bearing the phen-PNI chromophoric ligand, measured using three different spectroscopic techniques, each from ultrafast to conventional time domains.[28] The MLCT excited state lifetime was increased approximately 3000-fold at room temperature with respect to that of the model complex [Re(phen)(CO)$_3$Cl] as a result of thermal equilibrium between the emissive ^{3}MLCT state and the long-lived triplet ligand-centered (^{3}LC) state on the PNI chromophore. This represented the longest excited state lifetime ($\tau = 650\ \mu s$) that has ever been recorded for a Re[I]-based MLCT photoluminescence at room temperature. The energy transfer processes and the associated rate constants leading to the establishment of the excited state equilibrium were elucidated by a powerful combination of three techniques (transient visible and infrared (IR) absorption and photoluminescence), each applied from ultrafast to the micro- or millisecond time scale. The MLCT excited state was monitored by transient IR using CO vibrations through time intervals where the corresponding signals obtained in conventional visible transient absorption were completely obscured by overlap with strong transients originating from the pendant
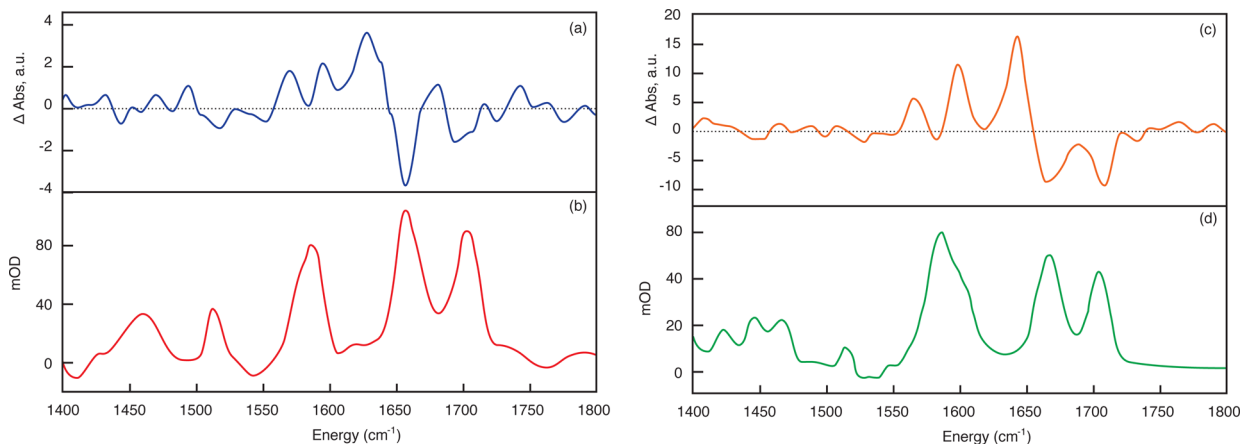
applied to MLCT chromophores was developed in numerous laboratories, and the interested reader is encouraged to seek out these representative reviews on the subject.[26,27] Following 355 nm pulsed (nanosecond) laser excitation, the two ground-state imide C=O bands in each compound were bleached, and two substantially lower energy vibrations were produced (Figure 3), with the lowest energy feature appearing as two distinct bands split by an overlapping transient bleach. Model studies performed on triplet sensitized PNI confirmed that the time-resolved vibrational data were consistent with photoinduced sensitization of the ^{3}IL (^{3}PNI-based) excited state. Density functional theory calculations supported the assignments in **9** and **10** because localization of triplet electron density on the PNI moiety was calculated to produce red-shifted C=O

Figure 3. TRIR difference spectra taken 1 μs after a 355 nm pulse for PNI (a) and **9** (c), as well as the respective FT-IR spectra (b, d), all recorded in CHCl$_3$. Adapted from ref 25.
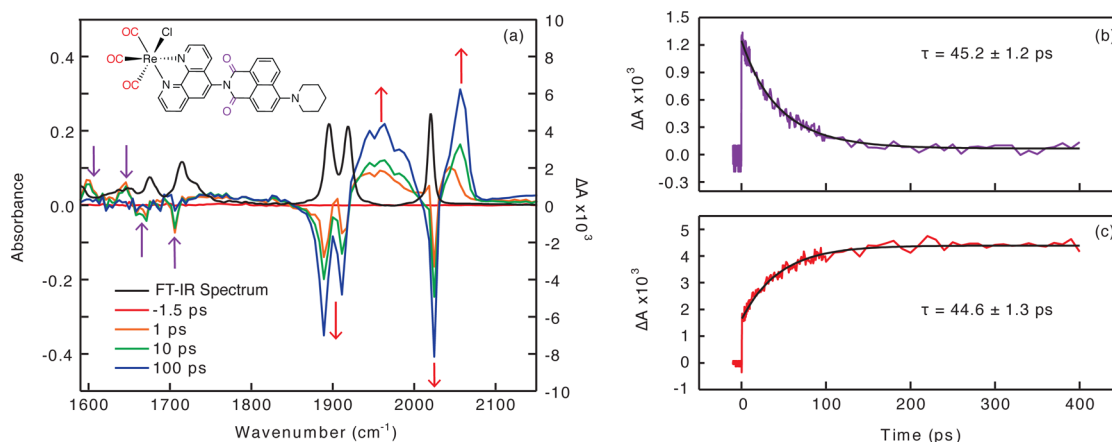
Figure 4. (a) Ground state FT-IR spectrum and time-resolved infrared difference spectra of **11** in THF following 400 nm pulsed laser excitation with single wavelength IR transients measured at 1645 cm^{-1} (b) and 1945 cm^{-1} (c). Adapted from ref 28.
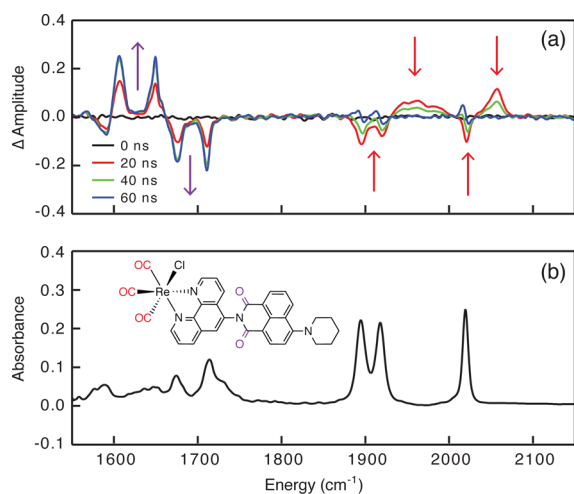

Figure 5. Time-resolved step-scan FTIR difference spectra of **11** following 410 nm pulsed excitation (a) and its ground state FT-IR spectrum in THF (b). Adapted from ref 28.

PNI chromophores, Figures 4 and 5.[28] Following initial excitation of the ^{1}LC state on the PNI chromophore, energy was transferred, producing the MLCT state with a time constant of 45 ps; the fit to the TRIR data is presented in Figure 5 although this time constant was confirmed in all three measurement domains within experimental error. Energy transfer from ^{1}PNI* to produce the ^{1}MLCT* excited state was confirmed by the agreement of Forster calculations with experimentally observed rates and transfer efficiencies. Intersystem crossing from the ^{1}MLCT to the ^{3}MLCT excited state was believed to be extremely fast and was not resolved in this investigation. Finally, triplet energy was transferred from the ^{3}MLCT to the PNI-centered ^{3}LC state in less than 15 ns, ultimately achieving equilibrium between these two excited states. Subsequent relaxation to the ground state occurred via emission resulting from thermal population of the ^{3}MLCT state with a resultant lifetime of 650 μs. Chromophore **11** therefore represents an interesting example of "ping-pong" energy transfer wherein photon excitation first migrates away from the initially prepared ^{1}PNI* excited state and then ultimately returns to this moiety as a long-lived excited triplet, which disposes of its energy by equilibrating with the photoluminescent Re^I MLCT excited state. We successfully applied a similar excited-state equilibrium

approach to extend the lifetimes of metal−metal-to-ligand charge transfer (MMLCT) excited states using PNI subunits in conjunction with d^8−d^8 Pt^{II} dimers in 2014.[29]

PHOTOPHYSICAL PROPERTIES AND DYNAMICS IN Pt^{II}-CONTAINING METAL−ORGANIC CHROMOPHORES

The group has maintained a continuous research effort in Pt^{II}-acetylide chromophores dating back to 2002. Our initial interest in this area related to the sensitization of ligand-localized phosphorescence in the appended acetylide chromophores, taking advantage of the enormous spin orbit coupling presented by the Pt^{II} metal center in direct conjugation with these ancillary subunits. Ultimately, we felt that such chromophores would enable a broad range of photoactivated bimolecular chemical reactions. Following the lead of Che,[30] Eisenberg,[31] and Schanze,[32] who evaluated the charge transfer excited states in numerous Pt^{II} diimine bis(acetylide) chromophores, Irina Pomestchenko from my laboratory prepared the first of these structures (**12**), which contained two pyrenylacetylides; these photophysical properties were directly compared with two model chromophores, **13** and **14**.[33] Compound **13** effectively models the charge transfer excited state in a prototypical Pt(diimine)-(C≡CR)$_2$ structural motif, whereas **14** deletes any contributions from the Pt → diimine charge transfer process while positioning two pyrenylacetylides in a *trans*-geometry, avoiding any possibility of intramolecular ground-state interactions between neighboring arylacetylides. Figure 6a displays the absorption spectra of **12**−**14** measured in MTHF. The pyrenylacetylide chromophores in **12** and **14** are largely responsible for the structured π−π* transitions between 350 and 400 nm. The visible absorption bands near 450 nm are assigned to Pt → diimine MLCT transitions and, although red-shifted, are qualitatively similar to **13**. The charge transfer assignment is consistent with the negative solvatochromic shifts observed for the low-energy absorption bands in **12** and **13**. The higher energy ligand-localized transitions between 350 and 400 nm, which arise from π−π* electronic transitions within the pyrenylacetylide fragments in **12** were not significantly perturbed by solvent polarity. Similar results were obtained for the structural model **14**, illustrating that the low energy pyrenyl-based π−π* transitions were truly ligand-localized and did not exhibit appreciable charge-transfer character.

Figure 7. Transient absorption difference spectra of **13** in MTHF following the 100 fs 400 nm excitation pulse (a) and the kinetic trace at 644 nm with the biexponential solid line fit superimposed with time constants of 200 fs and 3.6 ps (b). Adapted from ref 34.
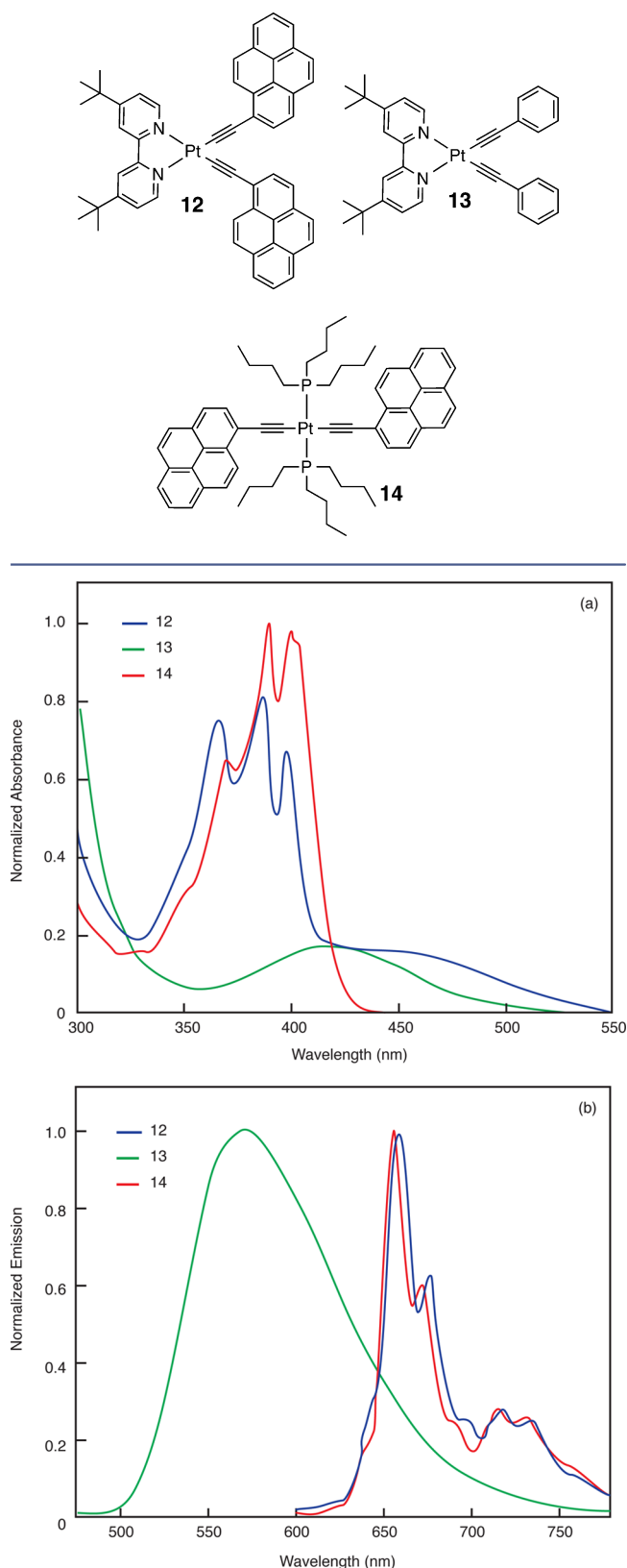

Figure 6. Normalized absorption (a) and photoluminescence (b) spectra for **12–14** in deaerated MTHF at room temperature. Adapted from ref 34.

The RT emission spectrum of **13** could be measured in aerated 2-methyltetrahydrofuran (MTHF), whereas the corresponding spectrum for **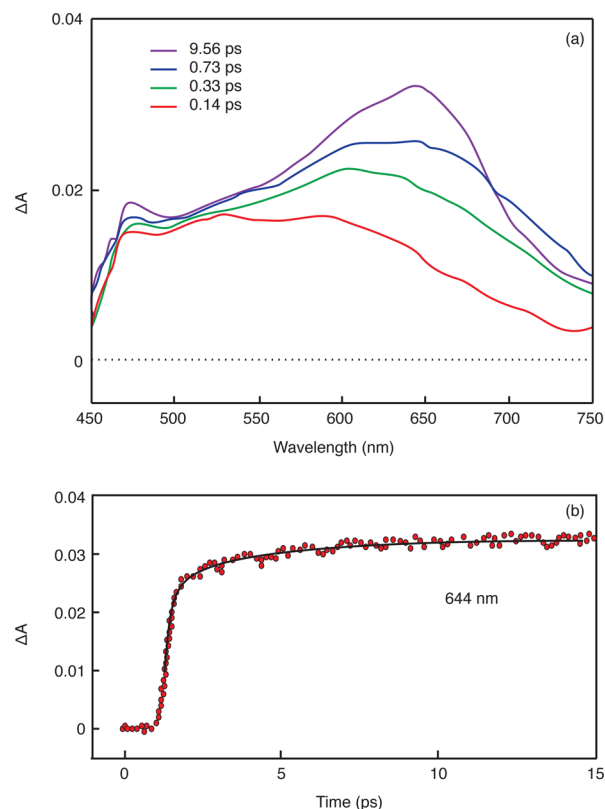12** was nearly quantitatively quenched by dissolved O_2, necessitating its removal, Figure 6b. The luminescence in **13** was shown to originate from a MLCT manifold whereas the emission from **12** was red-shifted (over 100 nm), structured, and relatively sharp by comparison and almost quantitatively matches the room-temperature phosphorescence exhibited by model **14**, Figure 6b. In the cases of **12** and **14**, the emissions were most consistent with ^{3}IL phosphorescence emanating from the pyrenylacetylide moiety. Work from the laboratory has also shown that selective excitation of the low energy CT transitions in **12** sensitizes the production of the ^{3}IL pyrenylacetylide-based phosphorescence in CH_2Cl_2 at 659 nm. Not surprising, the results obtained in MTHF were essentially identical in emission maximum (658 nm) and spectral profile, illustrating that the minor modification in solvent polarity did not affect the nature of the lowest ^{3}IL excited state in these molecules.

Given these novel photophysical properties, we decided to embark on ultrafast experiments to glean insight into how fast energy flowed to the ^{3}IL excited state from the initially prepared excited state and what potential intermediates were involved.[34] Subsequent to 400 nm excitation, formation of the charge transfer excited state in **13** was complete within 200 fs, Figure 7, while intersystem crossing to the ^{3}IL excited state in **14** occurred with a time constant of 5.4 ps, Figure 8. These combined results were not very surprising given the nature of literature data at that point in time. However, selective excitation into the low-energy CT bands in **12** led to the formation of the ^{3}IL excited state with a time constant of 240 fs, suggesting ultrafast wire-like energy migration in this molecule, Figure 9. These kinetic data implied that the presence of the charge transfer states in **12** markedly
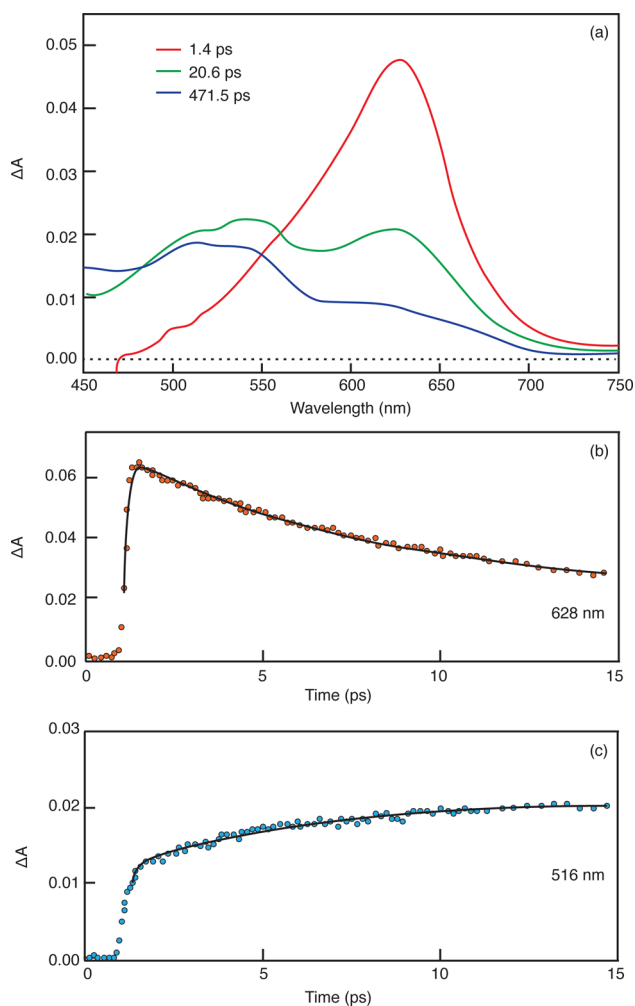
Figure 8. Transient absorption difference spectra of **14** in MTHF following a 100 fs, 400 nm excitation pulse (a) and the kinetic traces at 628 and 516 nm with their multiexponential solid line fits superimposed (b, c). Adapted from ref 34.
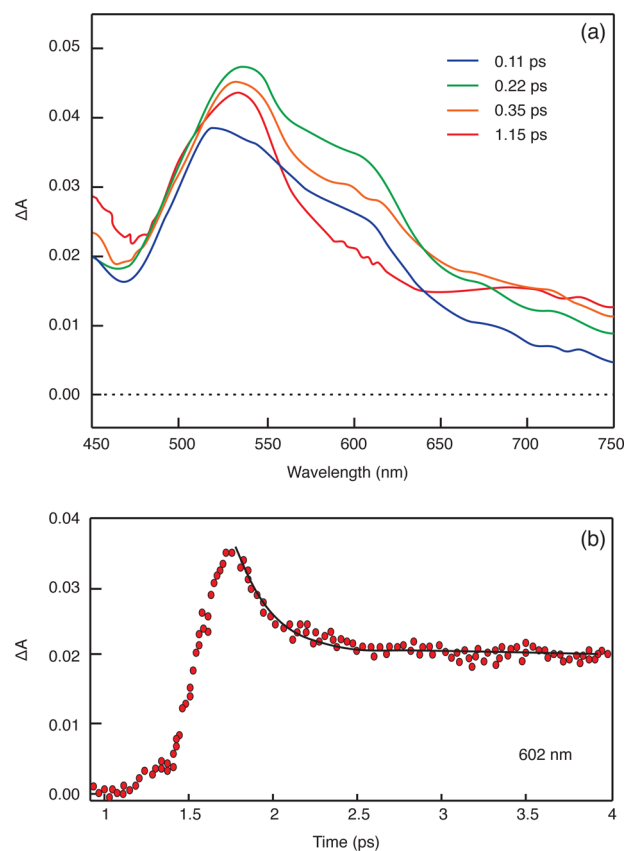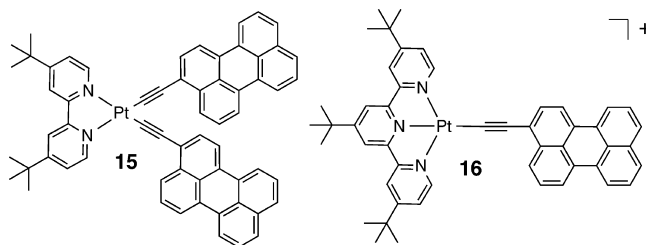

Figure 9. Transient absorption difference spectra of **12** in MTHF at several delay times following a 100 fs, 400 nm excitation pulse (a) and the absorption transient recorded at 602 nm (b). Adapted from ref 34.

accelerated the formation of the triplet state of the pendant pyrenylacetylide ligand. In essence, the triplet sensitization process was kinetically faster than pure intersystem crossing in **14** as well as vibrational relaxation in the CT excited state of **13**. These results strongly suggested that the presence of the CT manifold enabled rapid triplet sensitization in **12** and demonstrated how rapidly energy can truly migrate in strongly electronically coupled structures containing many overlapping potential energy surfaces.

Our interests in expanding the nature of the acetylide chromophores in these molecules led to the development of the Pt^{II} peryleneacetylides **15** and **16**,[35] and eventually the perylenediimide acetylides **17**–**20**.[36−38] In terms of the perylenediimide (PDI) molecules, we discovered that when linked to the Pt^{II} center, the acetylide linkage projecting from the bay position (this refers to the carbon atoms located on the interior of the aromatic system resembling a docking bay) of the PDI chromophore readily promoted formation of its ^{3}IL excited state.[36] It should be noted that in a related study, direct coupling of PDI to a Pd^{II} center through a metal−carbon σ-bond failed to generate this desirable outcome.[39] Upon ligation to the Pt^{II} center, the bright singlet-state fluorescence (Φ = 0.91, τ = 4.53 ns) of the free PDI-CCH chromophore

(terminal acetylene model chromophore) was quantitatively quenched and no long wavelength photoluminescence was observed from any of the Pt^{II}−PDI complexes in deaerated solutions. Ultrafast transient measurements revealed that upon ligation of PDI-CCH to the Pt^{II} center in **17**, picosecond intersystem crossing (τ = 2−4 ps) from the ^{1}PDI excited-state was followed by vibrational cooling (τ = 12−19 ps) of the hot ^{3}PDI excited state, Figure 10.[37] In the terpyridyl structure **20**, similar transient spectroscopic behavior was observed with respect to the bipyridyl analog, however, we decided to evaluate the step-scan transient IR spectroscopic behavior of this molecule in MTHF due to improved photostability in this solvent.[38] Molecule **20** exhibited strong (ε ≈ 5 × 10^4 M^{-1} cm^{-1}) low energy PDI acetylide-based π−π* absorption bands in visible range extending to 600 nm, while producing highly quenched singlet fluorescence (Φ = 0.014 ± 0.001, τ = 109 ps) with respect to the nonmetalated PDI model chromophore. Nanosecond transient absorption spectroscopy revealed the presence of a long excited state lifetime (372 ns in MTHF)
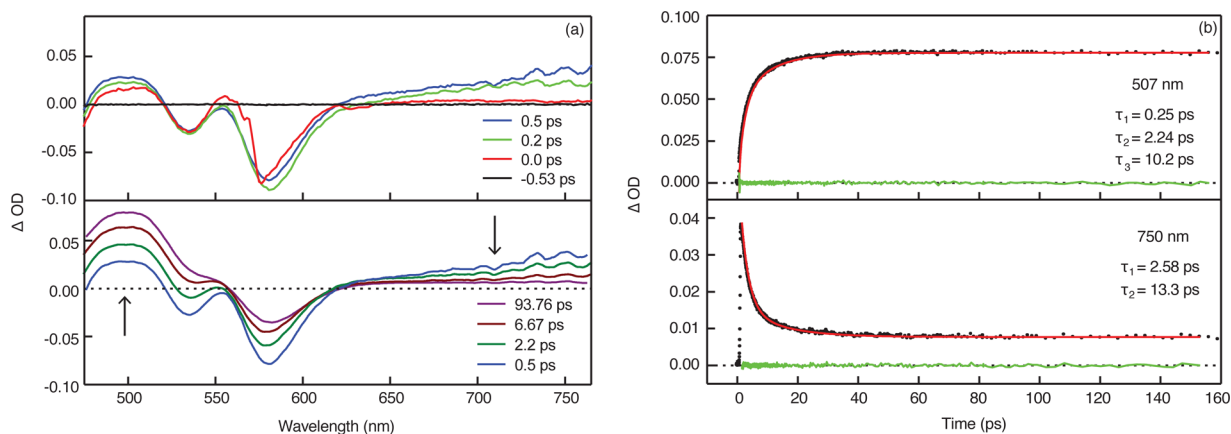
Figure 10. Picosecond transient absorption difference spectra of **17** in CH$_2$Cl$_2$ at selected delay times (a) and single-wavelength kinetic traces (black) with corresponding fits (red) superimposed (b) and residuals (green). Adapted from ref 37.
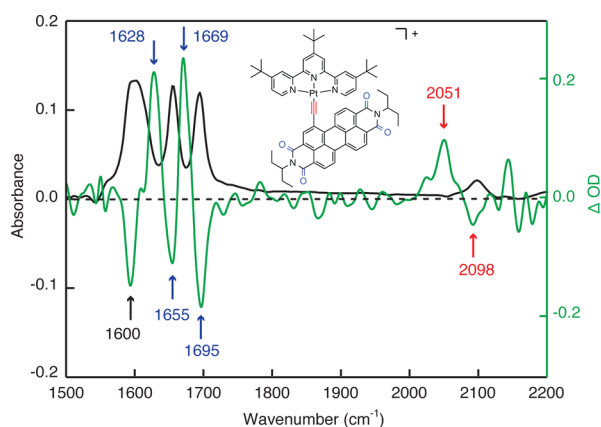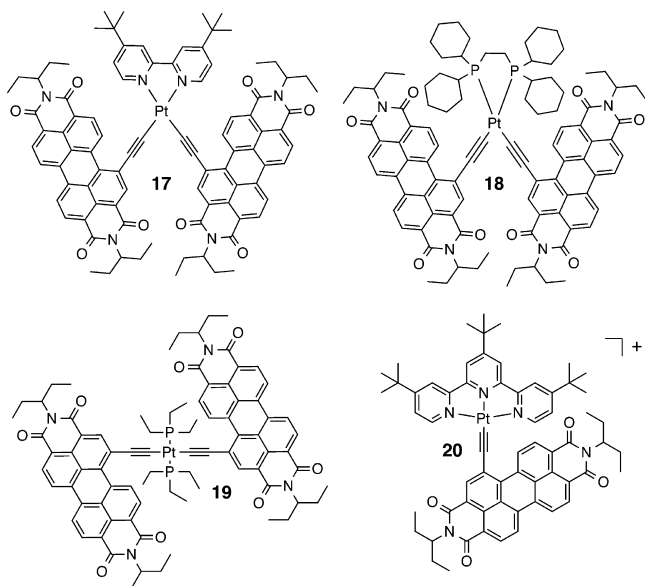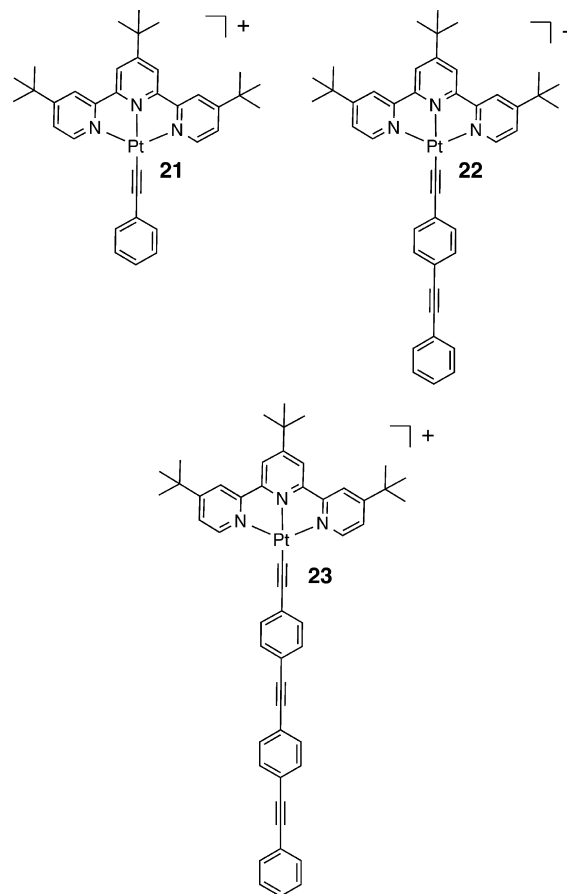

Figure 11. Ground-state FTIR spectrum (black) and time-resolved step-scan FT-IR difference spectrum (green) of **20** in DCM at 50 ns delay following 532 nm pulsed excitation. Adapted from ref 38.

used to characterize the triplet excited state of the PDI-acetylide sensitized in **20** in this study, Figure 11. The observed red shifts (∼30−50 cm^{-1}) in the C=O and C≡C vibrations of **20** in the long-lived excited state were consistent with the formation of the ^{3}PDI acetylide state and were found to be in excellent agreement with the expected change in the relevant DFT calculated IR frequencies in the nonmetalated PDI model chromophore's ground singlet state and lowest triplet excited state.

The rich photophysical properties of Pt^{II} terpyridyl aryl-(acetylide) chromophores have been widely developed by a number of researchers,[40−43] and the Yam group in particular has made many notable contributions; only a few are cited here

with transient features consistent with the PDI−acetylide triplet state, ascertained by direct comparison to a model Pt^{II} PDI−acetylide complex lacking low energy charge transfer transitions. Time-resolved step-scan FT-IR spectroscopy was
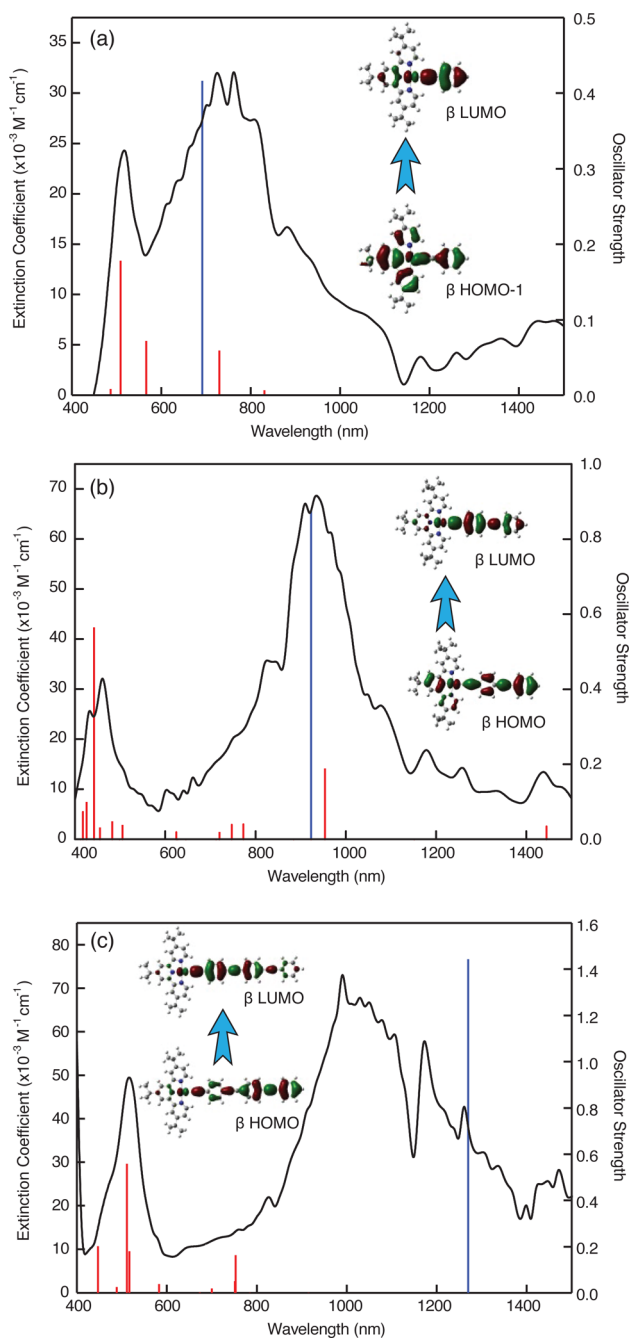
Figure 12. Calculated oscillator strengths (red and purple vertical lines) of the transient excited state of **21** (a), **22** (b) and **23** (c) and the experimental difference spectra taken at a delay of 100 ns following a 470 nm laser pulse. The orbitals involved in the strongest red-to-near-IR transition (purple vertical lines) are presented. Adapted from ref 49.

due to space limitations.[44−47] Our interest in these molecules has been largely related to understanding their excited state absorption properties.[48] In a recent study, three Pt[II] terpyridyl acetylide charge transfer (CT) complexes possessing a lone ancillary ligand systematically varying in phenylacetylide (PA) π-conjugation length, $[Pt(^tBu_3tpy)([C{\equiv}C-C_6H_4]_n-H)]ClO_4$ (n = 1, 2, or 3) were investigated to evaluate their suitability for deployment in optical power limiting applications.[49] DFT calculations performed on the ground states of complexes **21**, **22**, and **23** revealed that their HOMOs reside mainly on the

ancillary π-conjugated PA moiety (86−97%) with LUMOs predominantly centered on the terpyridyl acceptor ligand (91−92%). This electronic structure led to the production of a triplet ligand-to-ligand CT ([3]LLCT) excited state upon visible light excitation with minor contributions from the corresponding [3]MLCT excited state. Unusually strong red-to-near-IR transient absorptions were produced in the excited states of these molecules following selective long wavelength visible excitation of the low energy CT bands that did not emanate from the terpyridyl radical anion produced in the CT excited state or from an arylacetylide-based triplet [3]IL excited state, Figure 12. These absorptions systematically red-shifted across the series indicating that they were likely related to the π-conjugation length in the ancillary ligand. A computational investigation using DFT and TDDFT methods revealed that the intense near-IR transient absorptions did indeed result from transient oxidation of the PA subunit. In essence, the production of the [3]LLCT excited state transiently oxidized the PA moiety by one electron, producing the corresponding highly absorbing radical cation-like species. The computational work successfully predicted the relative oscillator strengths and peak wavelengths of the measured excited state absorption transients across this series of molecules, whose transitions resemble that of the open shell PA radical cation species.

■ CONCLUSIONS

The metal−organic structural motif presents numerous opportunities for the manipulation of photophysical properties through exploitation of the desirable features of each component. Molecules can be constructed with designer light-harvesting properties, tunable excited state lifetimes and photoluminescence spectra, as well as controlled excited state absorption properties. The available molecular toolbox for the generation of new structures exhibiting interesting photophysical properties appears limitless and simply requires the continued ingenuity of researchers. The application of dynamic spectroscopic techniques including transient absorption, transient infrared, transient Raman, time-resolved fluorescence/photoluminescence, as well as emerging 2D optical techniques to these chromophores will continue to glean fundamental insight into their underlying photophysics while navigating future molecular design principles of metal−organic chromophores.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biography

Felix (Phil) Castellano earned a B.A. in Chemistry from Clark University in 1991 and a Ph.D. in Chemistry from Johns Hopkins University in 1996. Following an NIH Postdoctoral Fellowship at the University of Maryland, School of Medicine, he accepted a position as Assistant Professor at Bowling Green State University in 1998. He was promoted to Associate Professor in 2004 and to Professor in 2006 and was appointed Director of the Center for Photochemical Sciences in 2011. In 2013, he moved his research program to North Carolina State University where he is currently a Professor in the Department of Chemistry. His present research focuses on metal−organic chromophore photophysics and energy transfer, photochemical upconversion phenomena, solar fuels photocatalysis, and excited state electron transfer processes.

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