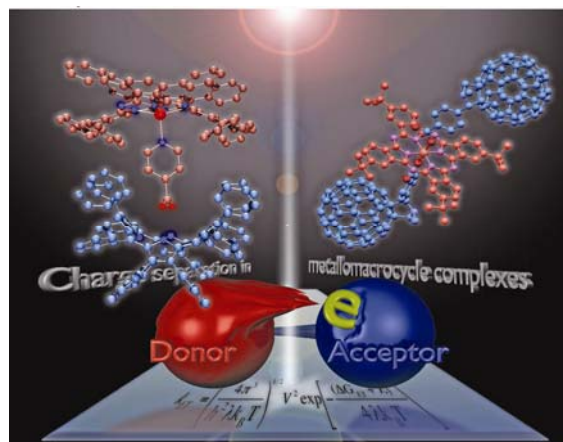
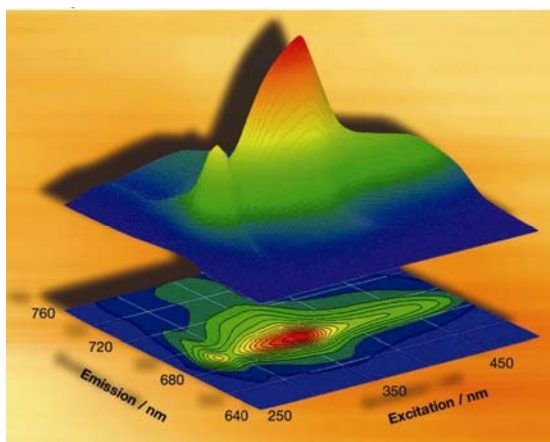


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[Pt(mesBIAN)(tda)]: A near-infrared emitter and singlet oxygen sensitizer†

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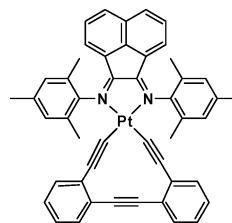
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The synthesis and subsequent photophysical investigation of [Pt(mesBIAN)(tda)], where mesBIAN is bis(mesitylimino)acenaphthene and tda is tolan-2,2'-diacetylide, reveal excited-state characteristics best described as triplet charge transfer (³CT) in nature upon visible light excitation. Large ground-state dipole moments are apparent as the absorption spectrum dramatically red-shifts with decreasing solvent polarity. The ³CT excited state is significantly lower in energy than the ligand-centered ³tda excited-state, as confirmed by steady-state and time-resolved techniques. Singlet oxygen sensitization studies demonstrate that ¹O₂ production occurs by diffusive quenching from the photo-excited ³CT state ($\Phi_{\Delta} = 0.24$, $\lambda_{\text{max}} \sim 1270$ nm) in oxygen-saturated dichloromethane.

Introduction

For nearly a decade and a half, fundamental and applied research has continued to expand and exploit the photochemistry and photophysics of platinum(II) polyimine acetylide complexes for a variety of applications such as optical power limiting, electroluminescence, singlet oxygen sensitization, cation sensing, vapo-chromism and luminescent probes.^{1–18} This large body of applications is a result of the rich photochemistry and photophysics presented by this molecular motif. Indeed, we have also demonstrated the ability to access long-lived excited states of pendant organic chromophores through use of this molecular platform.^{19–21}

Recent efforts have begun to explore the ability to shift the charge transfer (CT)-based electronic transitions of Pt(II) chromophores to lower energy by incorporating diimine ligands with lower π^* accepting orbitals. This has led to the design of platinum molecules with absorption and emission photophysics extending into the red- and near-IR portions of the electromagnetic spectrum. Use of such ligands such as bis(mesitylimino)acenaphthene (mesBIAN) shift the charge-transfer transition to much lower energy while the remaining two coordination sites of Pt(II) can be occupied by acetylide ligands for further electronic manipulation and design.^{12,22} To this end, we report a new Pt(II) metallacycle whose structure is shown below, exhibiting substantial solvent-dependent shifts in both absorption and emission spectra. Steady-state and time-resolved spectroscopy are employed to elucidate the nature of the excited-states exhibited by these complexes, while singlet oxygen sensitization is also demonstrated to be productive.



Experimental

All reactions were carried out under an inert and dry argon atmosphere using standard techniques. Anhydrous CH₂Cl₂ and diisopropylamine suitable for synthesis were freshly distilled over CaH₂. All other reagents from commercial sources were used as received. ¹H NMR and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. All chemical shifts are referenced to the residual solvent signals previously referenced to TMS and splitting patterns are designated as s (singlet), d (doublet) and m (multiplet). Routine EI mass spectra (70 eV) were measured in-house using a direct insertion probe in a Shimadzu QP5050A spectrometer. MALDI-TOF mass spectra were acquired using a Bruker-Daltonics Omnicflex spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparations

Di-*o*-bromotolane,²³ bis-*o*-((trimethylsilyl)ethynyl)tolane,²⁴ di-*o*-ethynyltolane ((OBET)H₂),²⁴ and Pt(mesBIAN)Cl₂¹² were synthesized according to literature procedures and yielded satisfactory mass and ¹H NMR spectra.

Pt(mesBIAN)(tda)

Pt(mesBIAN)Cl₂ (100 mg, 0.1465 mmol) and CuI (0.3 mg, 0.016 mmol) were placed in a sealable reaction vessel. A solution of CH₂Cl₂ and diisopropylamine (5:1) (60 mL) was degassed for 15 min and added to the flask. An excess (OBET)H₂ (226 mg, 1 mmol) was added to the reaction mixture and the reaction

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† Electronic supplementary information (ESI) available: Cyclic voltammograms, 77 K emission, and transient decays with single exponential fits. See DOI: 10.1039/b818177b

mixture was sealed with a Teflon screw-cap fitted with an o-ring and stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue was obtained as a dark orange powder. The powder was dissolved in CH_2Cl_2 , washed with H_2O , and the organic fractions were dried over MgSO_4 . Evaporation of CH_2Cl_2 gave a brown powder. Purification by chromatography on alumina eluting with CH_2Cl_2 yielded the product as a deep dark-purple microcrystalline solid (90 mg, 73%). $^1\text{H NMR}$ (CDCl_3): δ 8.18 (d, 2H), 7.56 (m, 2H), 7.48 (m, 2H), 7.18 (s, 4H), 7.13 (m, 2H), 7.05 (m, 2H), 7.00 (d, 2H), 6.94 (m, 2H), 2.54 (s, 6H), 2.41 (s, 12H). MALDI-MS: m/z 836. Anal. Calc. for $\text{C}_{48}\text{H}_{36}\text{N}_2\text{Pt}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 66.32; H, 4.22; N, 3.19. Found: C, 65.93; H, 4.25; N, 3.19%.

Photophysical measurements

Static UV-Vis absorption spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer, accurate to ± 2 nm. Corrected steady-state luminescence spectra were obtained by a PTI Instruments spectrofluorimeter equipped with a Peltier-cooled InGaAs detector using lock-in detection. This fluorometer operates under the control of FeliX32 software from PTI. A Melles Griot Series 74 HeCd laser was used as the excitation source where the 442 nm output (50 mW) was directed into the PTI spectrofluorimeter sample chamber. The laser power was measured with a Molectron Power Max 5200 power meter. All photophysical measurements were conducted at ambient temperature, 22 ± 2 °C, unless otherwise stated. Solutions prepared for all photophysical experiments were optically dilute for steady-state photoluminescence ($\text{OD} = 0.09\text{--}0.11$) and for emission lifetime determination ($\text{OD} = 0.01$) whereas nanosecond transient absorption experiments utilized higher concentrations ($\text{OD} = \sim 0.4$). All spectroscopy samples were prepared with spectroscopic grade solvent in 1 cm^2 anaerobic quartz cells (Starna Cells), degassed by solvent-saturated high purity argon for at least 35 min prior to the measurements and maintained under argon atmosphere throughout the experiments. Emission quantum yields of $[\text{Pt}(\text{mesBIAN})(\text{tda})]$ in various solvents were determined relative to $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$ in CH_3CN ²⁵ and values reported herein represent an average of at least three independent measurements. Singlet oxygen quantum yield measurements were determined relative to perinaphthenone²⁶ and reported values represent an average of at least three independent measurements.

Emission-corrected transient absorption and time-resolved emission spectra were collected on a Proteus spectrometer (Ultrafast Systems) equipped with a 150 W Xe-arc lamp (Newport), a Bruker Optics monochromator equipped with two diffraction gratings blazed for visible and near-IR dispersion, respectively, and Si or InGaAs photodiode detectors (DET 10A and DET 10C, Thorlabs) optically coupled to the exit slit of the monochromator. Time-resolved emission spectra were corrected for detector responsivity. Excitation at 535, 550 and 670 nm (CH_3CN , CH_2Cl_2 and toluene solution, respectively) with a power of 2.5 mJ pulse^{-1} from a computer-controlled Nd:YAG laser/OPO system from Oportek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an optical absorbance of 0.4 at the excitation wavelength. The data consisting of a 128-shot average were analyzed by Origin 8.0 software.

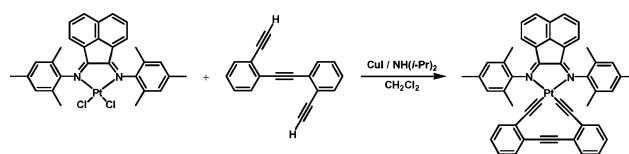
Electrochemical measurements

Cyclic and differential pulse voltammetry experiments were performed in CH_2Cl_2 solutions with $0.15\text{ M } n\text{Bu}_4\text{NPF}_6$ (TBAPF₆) as supporting electrolyte at room temperature. Platinum disk working, platinum wire auxiliary and Ag/AgCl (3 M NaCl) reference electrodes were used for all electrochemical measurements. CH_2Cl_2 was of spectroscopic grade for all electrochemistry experiments and TBAPF₆ was recrystallized from ethanol a minimum of three times. The solutions were degassed with argon prior to each measurement. The ferrocenium–ferrocene couple ($\text{FcP}_2^{+/0}$) was used as an internal reference. All voltammograms were recorded at room temperature with a Bioanalytical Systems Epsilon controller interfaced to a Pentium PC.

Results and discussion

Preparation and structural characterization

The title chromophore, $[\text{Pt}(\text{mesBIAN})(\text{tda})]$, was synthesized and purified using routine standard procedures, Scheme 1.^{5,10,22,27} The final product is isolated in good yield as a deep-purple air-stable solid that is readily soluble in a range of polar and nonpolar organic solvents. The complex has been structurally characterized by a variety of techniques including NMR, mass spectrometry and elemental analysis, all of which agree with the proposed square-planar structure. Previous studies on the corresponding model chromophores $[\text{Pt}(\text{mesBIAN})\text{Cl}_2]$ ¹² and $[\text{Pt}(\text{dppp})(\text{tda})]$ ²⁷ are referenced for purposes of discussion on the nature of the ground and excited state structure of the title chromophore.



Scheme 1 Synthetic route for the production of $[\text{Pt}(\text{mesBIAN})(\text{tda})]$.

Electrochemistry

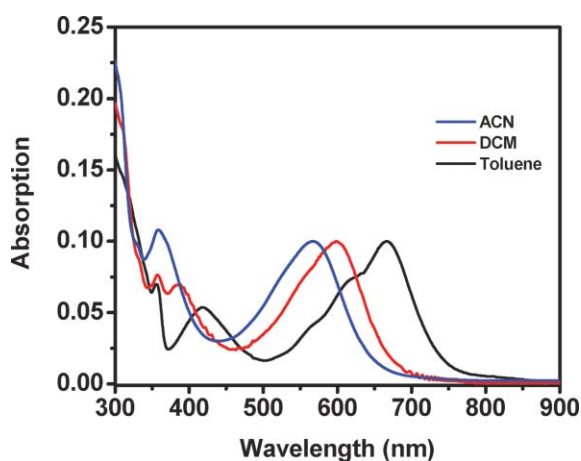
Cyclic and differential pulse voltammograms (see ESI†) were obtained in CH_2Cl_2 using a Ag/AgCl (3 M NaCl) reference electrode. $[\text{Pt}(\text{mesBIAN})(\text{tda})]$ displays a reversible ($i_{pc}/i_{pa} \sim 1$) mesBIAN-based one-electron reduction at $-0.70\text{ V vs. Ag/AgCl}$. This reduction potential is well within the expected range for the mesBIAN ligand as previously investigated Pt(II) chromophores incorporating this charge-transfer ligand typically exhibit reversible one-electron reductions from -0.6 to -0.8 V vs. SCE .^{12,22,28} An ill-defined irreversible oxidation occurs at $+1.30\text{ V vs. Ag/AgCl}$ and is attributed to the oxidation of the HOMO which is likely of combined Pt(II) and tda character. This is well within the expected oxidation range for Pt(II) charge-transfer complexes bearing acetylide linkages.^{10,27} The cyclic voltammetry data further reveal a significantly smaller HOMO–LUMO energy gap relative to similar bipyridyl systems, which is largely a consequence of the mesBIAN ligand being more easily reduced than di-*tert*-butyl bipyridine (dbbpy).²⁷

Table 1 Photophysical properties in different solvents at 298 K

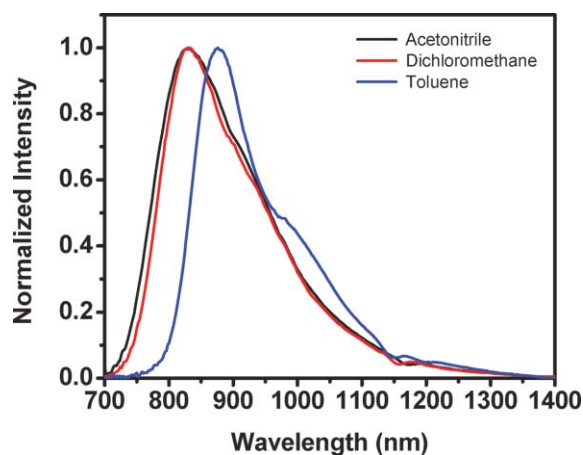
Solvent	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{em}} (\pm 5\%)$	$\tau_{\text{em}}/\text{ns}$	$10^{-4}k_{\text{r}}/\text{s}^{-1}$	$10^{-7}k_{\text{nr}}/\text{s}^{-1}$
CH ₃ CN	568	832	0.0015	39 ± 2	3.85	2.55
CH ₂ Cl ₂	598	832	0.0016	43 ± 2	3.72	2.31
Toluene	667	876	0.0012	28 ± 2	4.28	3.56

Absorption and emission properties

The spectroscopic properties measured for [Pt(mesBIAN)(tda)] in three different solvents are collected in Table 1. Fig. 1 presents the absorption spectra of [Pt(mesBIAN)(tda)] plotted as absorption vs. wavelength to best facilitate spectral comparisons. The higher energy features ($\lambda < 350$ nm) which are not solvent sensitive are attributed to $^1\pi\pi^*$ transitions of the mesBIAN and tda ligands. The absorption features at 358 and 567 nm in acetonitrile shift to lower energy in CH₂Cl₂ (384 and 600 nm, respectively) and further red-shift in toluene (418 and 667 nm, respectively). These shifts in energy can be easily observed by the naked eye as the solution color changes from purple, to blue, and finally to green, as illustrated in the TOC graphic. The apparent negative solvatochromism has been demonstrated by us and others to be a result of the large ground-state dipole moment in direct opposition to that of the excited state, commonly observed in related systems.^{4,10,17,27,29} The ground-state absorption in CH₂Cl₂ is significantly red-shifted compared to that of the recently reported non-macrocyclic analogue ($\lambda_{\text{max}} = 527$ nm).²² This was previously observed and ascribed to significantly increased σ -donation of tda electron density to the Pt(II) center in the bipyridyl analogues.²⁷ A similar mechanism of electronic interaction is expected to be operative here. Hence, the ^1CT absorptions in [Pt(mesBIAN)(tda)] contains significant contributions from the metallacyclic acetylide ligand.

**Fig. 1** Absorption spectrum of [Pt(mesBIAN)(tda)] displaying negative solvatochromism in CH₃CN, CH₂Cl₂ and toluene.

As a result of the red-shifted ground-state absorption, [Pt(mesBIAN)(tda)] readily displays photoluminescence which is correspondingly shifted into the near-infrared portion of the spectrum (Fig. 2). Solvatochromic shifts are also observed in the corrected emission spectra ranging from $\lambda_{\text{em}} = 832$ to $\lambda_{\text{em}} = 876$ nm, although the solvent effect is attenuated substantially in these emissions. Although the emission maximum does not

**Fig. 2** Near-infrared emission spectra of [Pt(mesBIAN)(tda)] in CH₃CN, CH₂Cl₂ and toluene.

shift between acetonitrile and dichloromethane, the onset of the emission is slightly red-shifted in CH₂Cl₂. The photoluminescence is assigned as ^3CT in all solvents as no detectable ligand centered emission from the tda ligand is observed at higher energy ($\lambda_{\text{em}} = 497$ nm).²⁷ The quantum yield for photoluminescence varies only slightly (0.0012–0.0016) across the three solvents, suggesting that the energy gap law is in complete control of excited state decay. Although the quantum yields are small, these values represent an order of magnitude increase relative to the [Pt(mesBIAN)Cl₂] precursor as well as the non-macrocyclic [Pt(mesBIAN)(CCPh)₂] analog.²² Inspection of the emission decay in each instance reveals single exponential lifetimes ranging from 28 to 43 ns, similar to that observed in related systems emanating NIR emission.^{30,31} In all solvents, the emission profiles decayed symmetrically and did not exhibit any unusual features. The lifetimes in conjunction with emission quantum yields can now be used to calculate radiative and nonradiative rate constants (Table 1) which are on the order of 10^4 and 10^7 s⁻¹, respectively. These rate constants conspire to produce an order of magnitude enhancement in the emission quantum yield of [Pt(mesBIAN)(tda)] relative to [Pt(mesBIAN)(CCPh)₂].²² Similar to previous studies, this enhancement may have origin in the added rigidity imposed by the tda ligand.^{10,27}

Although the excited state lifetimes are relatively short compared to more traditional Pt(II) acetylide charge-transfer chromophores,^{6,10,17,19,21,27} modest $^1\text{O}_2$ sensitization is indeed possible through bimolecular triplet–triplet energy transfer to ground-state $^3\text{O}_2$, Fig. 3. Upon air equilibration and subsequent oxygen saturation of the dichloromethane solution, the emission intensity of [Pt(mesBIAN)(tda)] is quenched by 25%. Stern–Volmer analysis indicates that ground-state $^3\text{O}_2$ quenches the [Pt(mesBIAN)(tda)] excited state with a rate constant (k_{q}) of 7.4×10^8 M⁻¹ s⁻¹ in CH₂Cl₂. Slightly larger k_{q} values were obtained in acetonitrile (2.53×10^9 M⁻¹ s⁻¹) and toluene (2.65×10^9 M⁻¹ s⁻¹), however, no discernable trend is observed. Shown in the inset of Fig. 3 is the low energy portion of the spectrum demonstrating the appearance of the typical phosphorescence of singlet oxygen ($^1\text{O}_2$) near 1270 nm. Quantification of this luminescence reveals that [Pt(mesBIAN)(tda)] readily sensitizes $^1\text{O}_2$ emission with $\Phi_{\Delta} = 0.24 \pm 0.01$. This is larger than the Φ_{Δ} values for related Pt(II) mesBIAN analogues, consistent with their corresponding shorter lifetimes in CH₂Cl₂. Given that percentage quenching and the

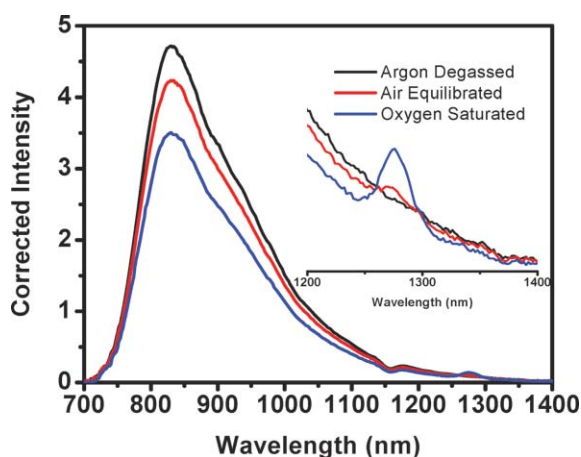


Fig. 3 Emission quenching and $^1\text{O}_2$ sensitization of [Pt(mesBIAN)(tda)] in CH_2Cl_2 .

Φ_{Δ} are quantitatively similar illustrates that $^1\text{O}_2$ sensitization can be directly correlated to the photoluminescence quenching in dichloromethane solution in this instance. In other words, all of the excited state quenching results in $^1\text{O}_2$ sensitization, implying 100% triplet energy transfer efficiency.

Fig. 4 displays the steady-state photoluminescence of [Pt(mesBIAN)(tda)] at room temperature and 77 K in 4 : 1 EtOH–MeOH. As the solution is cooled, a blue-shift in the emission maximum is observed along with increased definition of vibronic features. The maximum shifts by 1970 cm^{-1} from 848 to 728 nm. This shift is typical of ^3CT emission emanating from Pt(II) charge-transfer chromophores.^{3,7,27} Importantly, the 77 K emission does not exhibit any characteristic tda-based ^3IL photoluminescence at 497 nm.²⁷ The final 77 K spectrum agrees remarkably well with that of [Pt(mesBIAN)Cl₂] (see ESI†) which serves here as a ^3CT model chromophore.¹² These photoluminescence results strongly suggest that the lowest energy excited state is characterized simply as ^3CT . That is, the ^3IL excited-state of tda is too high in energy and/or simply inaccessible from the much lower lying ^3CT state. Hence, the transient absorption difference spectra should definitively produce the characteristics of the lowest energy ^3CT excited state.

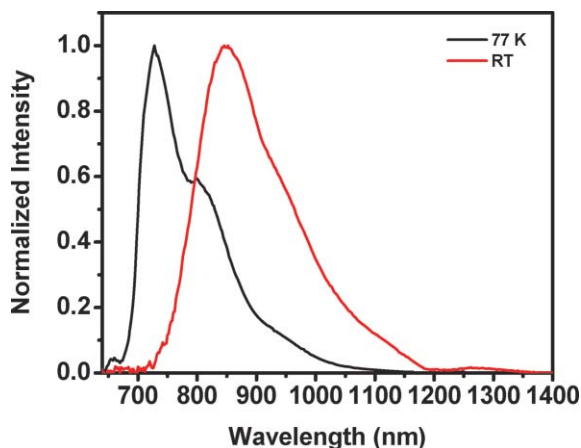


Fig. 4 Temperature-dependent emission spectra of [Pt(mesBIAN)(tda)] in 4 : 1 EtOH–MeOH measured at RT and 77 K.

Nanosecond transient absorption spectroscopy

Transient absorption difference spectra of [Pt(mesBIAN)(tda)] in selected solvents and at variable time delays following visible nanosecond pulsed laser excitation are given in Fig. 5. The current data provides the emission corrected absorption difference profiles between 360 and 1400 nm. The features displayed in the transient absorption difference spectra of [Pt(mesBIAN)(tda)] are sensitive to the solvent of choice in the experiment. Generally, the spectrum can be described by two ground-state bleaches overlapping with an excited-state absorption in the UV-Vis region of the spectrum. This is followed by a broad featureless excited-state absorption extending from the red portion of the visible spectrum out into the near-IR. In every case, the excited-state absorptions and ground-state bleaches self-consistently recover to the baseline and exhibit single exponential kinetics that quantitatively match the time-resolved photoluminescence data (see ESI†), indicating that no self-quenching occurs at the higher concentrations ($\sim 10^{-5}\text{ M}$) used for transient absorption studies compared to photoluminescence lifetime concentrations ($\sim 10^{-7}\text{ M}$).

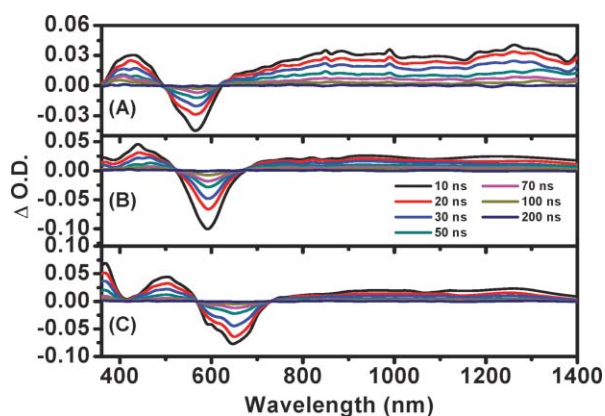


Fig. 5 Transient absorption difference spectra of [Pt(mesBIAN)(tda)] in CH_3CN (A), CH_2Cl_2 (B) and toluene (C).

In acetonitrile (Fig. 5A), the ground-state bleaching features observed at ~ 360 and 570 nm are in perfect alignment with the ground-state absorption features assigned to the ^1CT transitions. An apparent excited state absorption with a maximum at 430 nm is difficult to resolve as it overlaps well with the ground-state bleaches. In agreement with the photoluminescence lifetime in acetonitrile, all transient features decay mono-exponentially with a lifetime of 38 ns . In CH_2Cl_2 (Fig. 5B), the ground state bleaches shift to lower energy, to 380 and 590 nm , respectively, while the apparent transient absorption maximum shifts to $\sim 450\text{ nm}$. Again, all transient decays agree with the photoluminescence lifetime, $\tau = 45\text{ ns}$. Finally, the toluene solution provides the most red-shifted ground-state bleaching features (Fig. 5C), in agreement with the static absorption spectrum. The bleaches now shift to 410 and 660 nm , respectively, while the apparent excited-state absorption maximum shifts to 500 nm . The excited-state lifetime determined from transient absorption ($\tau = 30\text{ ns}$) again agrees very well with that of emission decay ($\tau_{\text{em}} = 28\text{ ns}$).

It is important to note that while the features present in the transient absorption spectra support the notion that the excited state is ^3CT in nature, features that are absent further imply that the higher energy ^3IL state of tda does not contribute any

influence (spectrally or temporally) to the lowest energy excited state of [Pt(mesBIAN)(tda)] which is best described simply as ³CT. Previous transient absorption studies demonstrated that the ³IL tda excited state features an intense excited state absorption centered at 440 nm with a lifetime of 12.1 μs in dichloromethane.²⁷ No significant spectral contribution at 440 nm in any solvent was resolved. Secondly, one would expect a significantly longer excited state lifetime if the ³IL tda state were involved in its decay which was not observed. Finally, the lack of any ³tda phosphorescence displayed at 77 K further eliminates any significant ³tda contribution within this Pt(II) metallacycle at room temperature or at 77 K. Hence, all excited state photophysics as well as ¹O₂ sensitization can be solely attributed to arising from the ³CT excited state.

Conclusions

In summary, a new Pt(II) low energy charge-transfer metallacycle incorporating the rigid tda ligand has been prepared and thoroughly characterized. This molecular design conceptually embodies the notion of supramolecular photochemistry as the individual bidentate ligand components substantially dictate the resultant spectroscopic properties when they are assembled together at a square-planar Pt(II) center. The photophysics of [Pt(mesBIAN)(tda)] has been directly compared to those of model chromophores from previous studies. Selective substitution of mesBIAN for dbbpy drastically decreases the ³CT energy while the rigidity of tda promotes larger emission quantum yields, longer lifetimes, and larger singlet oxygen production yields relative to previously examined Pt(II)-based near-IR emitters. Electrochemical results confirm a small HOMO–LUMO energy gap between the HOMO and mesBIAN π* acceptor orbitals. This small energy gap leads to substantially red-shifted absorption and near-infrared emission in all solvents investigated. Concomitant with large ground-state dipole moments, drastic solvatochromic effects are observable as the lowest energy absorption band shifts ~100 nm changing the color of the solutions from purple to blue to green. Although the excited state lifetime is shorter than typical Pt(II) charge-transfer chromophores bearing acetylide subunits, this NIR emitter is sufficiently long lived for bimolecular photoinduced chemistry as illustrated by the sensitization of ¹O₂ emission derived from efficient triplet–triplet energy transfer with dissolved O₂. The ³CT nature of the lowest energy excited state is further supported by low-temperature emission in addition to nanosecond transient absorption studies and in all cases no evidence for ³tda involvement in the excited state could be observed. This contribution has extended the use of the tda ligand into a chromophore exhibiting near-IR emission from a “pure” ³CT excited state which ultimately can be utilized for more creative excited-state photochemical schemes.

Acknowledgements

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