

Solvent-induced configuration mixing and triplet excited-state inversion: insights from transient absorption and transient dc photoconductivity measurements

Chunxing She,^a Aaron A. Rachford,^b Xianghuai Wang,^b Sébastien Goeb,^b Ala'a O. El-Ballouli,^b Felix N. Castellano^{*b} and Joseph T. Hupp^{*a}

Received 6th May 2009, Accepted 11th June 2009

First published as an Advance Article on the web 13th July 2009

DOI: 10.1039/b908977b

Solvent-induced excited-state configuration mixing in a Pt(II) diimine chromophore with phenylene ethynylene containing acetylide ligands, [Pt(^tBu₂bpy)(PE3)₂] (**1**), was characterized by nanosecond transient absorption spectroscopy and transient dc photoconductivity (TDCP). The mixing is a result of closely spaced triplet charge transfer (³CT) and intraligand-localized (³IL) triplet energy levels that are finely tuned with solvent polarity as ascertained by their parent model chromophores [Pt(^tBu₂bpy)(PE1)₂] (**2**) and [Pt(P2)(PE3)₂] (**3**), respectively. The absorption difference spectrum of the mixed triplet state is dramatically different from those of the ³CT and ³IL state model chromophores. The ³CT, ³IL and configuration-mixed triplet states led to distinct TDCP signals. The TDCP response is of negative polarity for ³CT excited states but of positive polarity for ³IL excited states. TDCP transients for **1** in mixed solvents are a combination of signals from the ³IL and ³CT states, with the signal magnitude depending on the polarity of solvent composition. The fraction of ³CT state character in the configurationally mixed excited state was quantified by TDCP to be ~0.24 in pure benzene, while it decreased to ~0.05 in 20 : 80 (v : v) benzene–CH₂Cl₂. The charge transfer fraction appears to increase slightly to ~0.11 in the lower polarity 20 : 80 *n*-hexane–CH₂Cl₂ medium. TDCP is shown to be a useful tool for the identification of the lowest excited state in electrically neutral metal–organic chromophores.

Introduction

For more than a decade, 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, vapochromism, and luminescent probes.^{1,2} This battery 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 platform.³ Of particular interest are compounds with energetically proximate triplet excited states poised for configuration mixing and state reordering. This motivation stems from the fact that molecules with closely spaced triplet charge transfer (³CT) and ligand-localized triplet (³IL) energy levels can be profoundly affected in terms of excited state decay relative to their parent model structures.^{2c,3a,4,5} While there has been progress attempting to establish ³CT–³IL

configuration mixing and state inversion for select molecules at room temperature,^{2b,5b} no clear-cut examples of triplet state crossover had been observed until the Pt(II) CT chromophore [Pt(^tBu₂bpy)(PE3)₂] (**1**) was reported by our group last year.^{3a} Compound **1** emerged as a result of rational structural design wherein recent synthetic advances coupled with explorations of molecular wire behavior in donor–bridge–acceptor compounds provided the necessary science related to conjugated bridge molecules that vary systematically in both singlet and triplet energy.⁶ Consistent with the fact that Pt(II) diimine chromophores have solvent controllable CT energy levels,^{2a,2b,5a} the appropriate combination of chromophores indeed led to the observation of solvent-induced triplet state inversion at room temperature in **1** as evidenced by static and dynamic photoluminescence in addition to preliminary nanosecond transient absorption studies.^{3a} Most importantly, our initial study included optical characterization of model chromophores [Pt(^tBu₂bpy)(PE1)₂] (**2**) and [Pt(P2)(PE3)₂] (**3**) which successfully mimic the ³CT and ³IL states in **1**, respectively (Chart 1).

In general, electrically neutral Pt(N[^]N)(C≡CR)₂ structures possess low energy absorption bands displaying strong negative solvatochromic behavior, a direct consequence of their polar ground states. The vectorial direction of this dipole can be considered in direct collinear opposition to the optical transition which produces the CT excited state, ultimately leading to an excited-state dipole moment close to

^a Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. E-mail: j-hupp@northwestern.edu; Fax: +1 847-467-1425; Tel: +1 847-491-3504

^b Department of Chemistry & Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403, USA. E-mail: castell@bgsu.edu; Fax: +1 419-372-9809; Tel: +1 419-372-7513

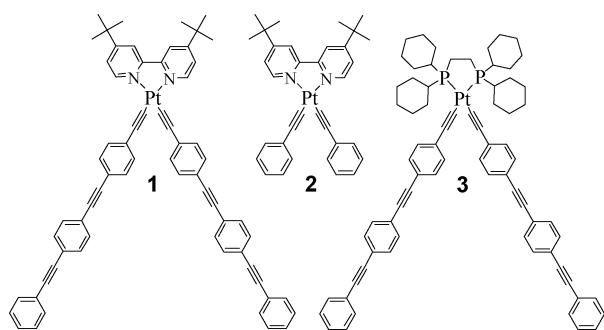


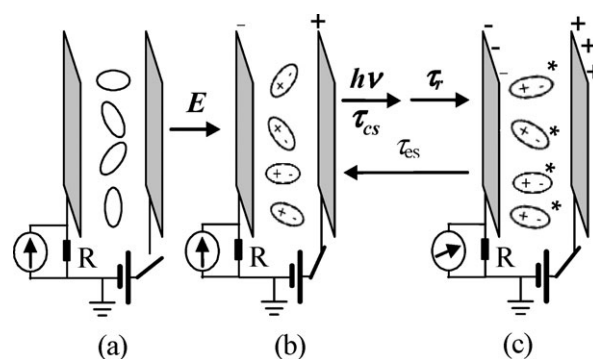
Chart 1 Molecular structures of [Pt(*t*Bu₂bpy)(PE₁)₂] (**1**), [Pt(*t*Bu₂bpy)(PE₁)₂] (**2**) and [Pt(P₂)(PE₃)₂] (**3**).

or equal to zero. Experimentally, the change in dipole moment resulting from photoexcitation of these structures can be directly interrogated using transient dc photoconductivity (TDCP).⁷ In addition, this technique can also be used in select chromophores to gauge molecular polarizability changes between the ground and excited states.⁸ As TDCP is amenable to neutral chromophores dissolved in relatively non-polar solvents, it is particularly well suited for studying the solvent-induced triplet state inversion in **1** which takes place across different mole fractions of dichloromethane in hexanes.^{3a} Given that the nature of the ³CT and ³IL excited states is so markedly distinct, one would anticipate quite different TDCP signals emanating from samples of **1** monitored as a function of solvent composition, similar to that observed in transient absorption difference spectra as described below. In this study, we used TDCP to successfully distinguish the ³CT and ³IL excited states in all three chromophores; the TDCP signals are negative in the case of ³CT excited states and positive when ³IL states are produced. Since chromophores **2** and **3** adequately model the ³CT and ³IL states in **1**, the TDCP signals of both excited state extremes were investigated in addition to the intermediate, configuration-mixed situations encountered in mixed solvent compositions in which **1** is dissolved.

Theory

The TDCP technique has been introduced previously.^{7,9} Here, we briefly summarize the necessary points that assist in understanding data interpretation. TDCP measures changes in solution electric polarization, ΔP , upon photoexcitation of a solute. These changes give rise to transient charge displacements that, in the presence of an externally applied electric field (E), can be detected capacitively with cell-defining conductive plates, see Scheme 1. The measured changes in polarization reflect differences in solute excited-state *versus* ground-state dipole moment—both the permanent dipole moment, $\Delta\mu$ ($= \mu_{\text{ES}} - \mu_{\text{GS}}$), and the field-induced dipole moment, $\Delta\mu^*$, which is the product of E and the change in molecular polarizability, $\Delta\alpha$ (or more precisely, the excess polarizability volume,¹⁰ $\Delta\alpha_V$). Assuming (for simplicity) that there is only one excited species, and that the solute does not strongly couple to the solvent,^{9b} the change in solute electric polarization depends on the time-varying excited-state concentration, $n_e(t)$, as follows:

$$\Delta P_{\text{solution}}(t) = \Delta P_{\text{solute}}(t) = n_e(t)E(\Delta\alpha + \frac{\Delta(\mu^2)}{3k_B T}) \quad (1)$$



Scheme 1 An illustration of the TDCP experiment. (a) Randomly oriented molecules in the absence of a field, (b) preferential orientation of molecular dipoles by an external electric field, (c) photoinduced charge separation (time = τ_{cs}) and further preferential molecular orientation (rotation; timescale τ_r). (c) Returns to (b) after decay of the excited states (time = τ_{es}).

where k_B is the Boltzmann constant, $\Delta\alpha = \alpha_{\text{ES}} - \alpha_{\text{GS}}$ and $\Delta(\mu^2) = \mu_{\text{ES}}^2 - \mu_{\text{GS}}^2$.

The analysis of TDCP data has been developed mainly for the case where signals arise from changes in *permanent* dipole moments.^{7,9b,11} We have recently adapted it to the interesting alternative case where signals arise in addition or instead from changes in polarizability, *i.e.* *induced* dipole effects. The transient voltage, $v(t)$, which is measured across the load resistor R in the circuit described in Scheme 1, results from the displacement current (where Q is charge), *i.e.* $v(t) = R \times dQ/dt$. The equation for time variation in the system is as follows:

$$v(t) + \tau_{\text{RC}} \frac{dv(t)}{dt} = RS \frac{dP}{dt} \quad (2)$$

where P is the polarization of solute, which is proportional to the excited-state population n_e , τ_{RC} is the RC time constant, and S is the surface area of the parallel measuring plates in the capacitance cell. Our analysis will consider only two states, *i.e.* the ground and lowest excited states.

For case 1, where the polarizability change ($\Delta\alpha$) is negligible compared to $\Delta(\mu^2)$:

$$v(t) + \tau_{\text{RC}} \frac{dv(t)}{dt} = RSE \frac{(\mu_{\text{ES}}^2 - \mu_{\text{GS}}^2) dn_e}{3k_B T dt} \quad (3)$$

For case 2, the polarizability change ($\Delta\alpha$) is measurable while $\Delta(\mu^2) = 0$.⁸

$$v(t) + \tau_{\text{RC}} \frac{dv(t)}{dt} = H\Delta\alpha \left[\frac{e^{\left(\frac{-t}{\tau_{\text{eff}}}\right)}}{\tau_{\text{eff}}} - \frac{e^{\left(\frac{-t}{\tau_{\text{es}}}\right)}}{\tau_{\text{es}}} \right] \quad (4)$$

In eqn (4), H is a constant experimental factor detailing the contributions of solvent and E , τ_{eff}^{-1} equals $\tau_{\text{es}}^{-1} + \tau_r^{-1}$ where τ_{es} and τ_r are the triplet lifetime and rotational diffusion time constant for the molecule being studied, respectively.

Experimental

The synthesis and luminescence characterization of molecules **1**, **2**, and **3** have been published elsewhere.^{3a} All photophysical

measurements were performed at ambient temperature in thoroughly deoxygenated spectroscopic grade solvents.

Nanosecond transient absorption spectrometry

Nanosecond transient absorption spectra were collected on a Proteus spectrometer (Ultrafast Systems) equipped with a 150 W Xe arc lamp (Newport), a Chromex monochromator (Bruker Optics) 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. The dispersion constant for both gratings is 5 nm mm^{-1} . Excitation at 355 or 475 nm with a power of 2.0–2.5 mJ per pulse from a computer-controlled Nd:YAG laser/OPO system from Opotek (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 and difference spectra at select delay times are presented.

Transient dc photoconductivity

All TDCP measurements were performed with instrumentation described previously.^{8,12} Briefly, a 1000 V potential was applied across a 0.30 mm gap between two electrodes. The samples were excited at 355 nm with the third harmonic of a Quantel Brilliant Nd:YAG laser (10 Hz). The 355 nm laser beam was expanded so that only the center part of the beam was sent through a $0.25 \text{ mm} \times 10 \text{ mm}$ slit. The pulse width was measured to be $\sim 5 \text{ ns}$ at half maximum with a 25 GHz Si photodiode (ET-2000 from Electro-optics technology, Inc.). Typical absorbed laser energies were *ca.* 3–10 μJ per pulse. Solution optical densities were between 0.4 and 1.2 at 355 nm. Solutions were deoxygenated before excitation. Reported values are averages from 2 to 4 repeated data sets. A typical data set comprised 10 to 20 measurements, each with an average of 256 shots. The RC time constant used was 1.0 ns *via* fits of experimental TDCP measurements of 4-dimethylamino-4-nitrostilbene (DMANS) in toluene as a standard, according to previously published work.^{7a} Analysis of the TDCP signal was aided by a fitting program kindly provided by Prof. Sergei Smirnov from NMSU. τ_r of the studied molecules was found to be $0.3 \pm 0.1 \text{ ns}$.

Results and discussion

Transient absorption of excited states with mixed configurations

The emission corrected nanosecond transient absorption (TA) difference spectra of all three chromophores at select delay times are presented in Fig. 1. The difference spectrum of **3** (Fig. 1A), which serves as the ³IL model chromophore, is characterized by ground-state bleaching near 350 nm and an intense excited-state absorption between 600 and 610 nm. Importantly, the difference spectrum is not significantly affected by solvent polarity as demonstrated by the overlaid spectra measured in neat dichloromethane and benzene solutions. This is consistent with our previous study where

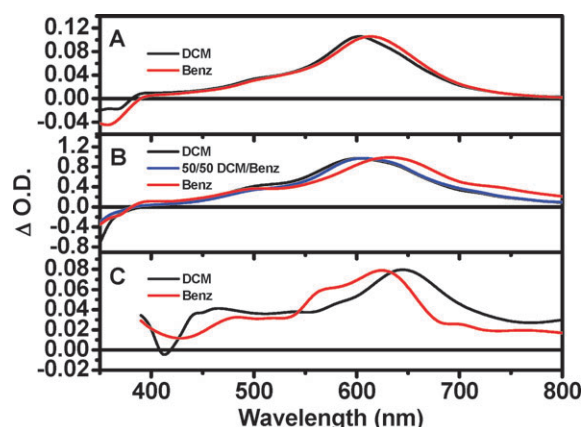


Fig. 1 Transient absorption difference spectra ($\pm 10 \text{ nm}$) of Pt(P2)(PE3)₂ measured at 1 μs (A), Pt(Bu₂bpy)(PE3)₂ at 1 μs (B), and [Pt(Bu₂bpy)(PE1)₂] at 0.1 μs (C) after a $\sim 7 \text{ ns}$ laser pulse. The solvent compositions are indicated in each panel. In panel B, the difference spectra have been normalized for comparison. The difference spectra in panels A and B were collected following 355 nm (2.5 mJ per pulse) excitation whereas the difference spectra in panel C were collected after 475 nm (2.0 mJ per pulse) excitation.

this chromophore exhibits a lowest ³IL excited state.^{3a} In contrast, the difference spectrum of **2** (Fig. 1C) which serves as our ³CT model chromophore is significantly affected by solvent polarity. Here, the ground-state bleach, which is overlapped with the excited-state absorptions, *red*-shifts from 415 to 430 nm with decreasing solvent polarity (CH₂Cl₂ to benzene solution). However, the excited-state absorption centered at $\sim 645 \text{ nm}$ in CH₂Cl₂ actually *blue*-shifts to $\sim 625 \text{ nm}$ in benzene. Assuming that the CT transitions in both instances terminate on a similar electronic state, the observed energy difference is consistent with a net decrease of the ³CT excited-state energy in the lower polarity solvent.

In an effort to understand further the solvent dependence of the lowest energy excited state of **1**, we plotted the excited-state absorption difference spectrum in three disparate solvents (Fig. 1B). The spectrum in dichloromethane agrees remarkably well with that of **3** in dichloromethane. The spectrum is characterized by ground-state bleaching near 350 nm and intense excited-state absorption centered near 600 nm. Consequently, the excited state is assigned as ³IL in dichloromethane, in agreement with our previous studies of steady-state emission and excited-state lifetimes.^{3a}

Upon decreasing the solvent polarity (from CH₂Cl₂ to benzene), the intense excited-state absorption *red*-shifts in energy from 600 to 630 nm. Note that if the nature of the excited state had remained ³IL, no significant shift in energy would have been observed (see Fig. 1A). The excited-state absorption maximum does *not* correlate to the ³CT excited-state absorption observed in benzene (see Fig. 1C), nor does the difference spectrum resemble a linear combination of ³IL and ³CT spectra. (A linear combination would be expected for two chromophores exhibiting an excited-state equilibrium.) Hence, the most reasonable assignment of the difference spectra in chromophore **1** is a configurationally mixed triplet excited state in agreement with our previous observations.

Distinct TDCP signals for the ^3CT and ^3IL states

TDCP measurements provide insights into the nature of the excited states, which, for **3** and **2**, are independent of solvent polarity. Fig. 2 shows TDCP signals for these two in benzene. From eqn (3) and (4), the shapes of the signals (amplitude *vs.* time) should closely approximate plots of the rate of change of the excited-state population ($\text{d}n_e/\text{d}t$) *versus* time. For an excited state that is long-lived ($>1\ \mu\text{s}$) relative to the 5 ns laser pulse (thin solid line in Fig. 1A), the signal's time profile resembles the Gaussian shape of the pulse. Upon excitation, the lowest excited states are long-lived ^3IL (65 μs) and ^3CT (1.1 μs) states for **3** and **2**, respectively,^{3a} and thus give rise to the Gaussian profiles. On the basis of the molecular geometry obtained by X-ray diffraction,¹³ and by placing a 2^+ formal charge on Pt and a 1^- formal charge on each of the two acetylide carbons that are bonded to Pt, both chromophores possess sizable dipole moments in the ground state.¹⁴ Accepting the formal charges at face value, we obtain a rough estimate of 10 D for the ground-state dipole moment.

Due to the $\pi-\pi^*$ nature of the lowest energy electronic transition, the dipole moment of **3** is not anticipated to change markedly upon excitation. However, by analogy to what we have observed for triplet states of porphyrin oligomers, the polarizability of **3** may be expected to increase upon population of the ^3IL excited state.⁸ Under these circumstances, eqn (4) predicts a positive TDCP signal for **3**—which is indeed observed experimentally (Fig. 2a). TDCP analysis gives an excess polarizability volume ($\Delta\alpha_V$) of $280 \pm 40\ \text{\AA}^3$ for the ^3IL state.

Consistent with the observed negative solvatochromism, the dipole moment of **2** should diminish upon MLCT excitation. Under these circumstances, eqn (3) predicts that the TDCP

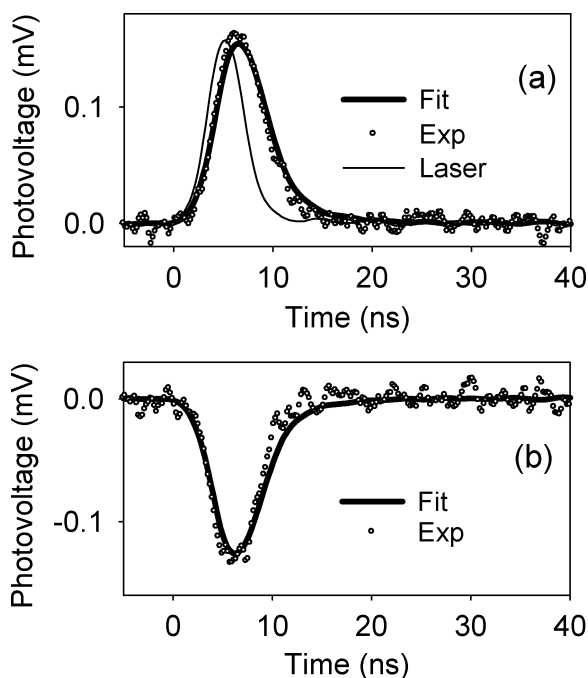


Fig. 2 TDCP signals for (a) **3** and (b) **2** in benzene as a result of excess polarizability change of **3** in the ^3IL state and of a reduced dipole of **2** in the ^3CT state, respectively.

signal for **2** will be negative¹⁴—and this is indeed borne out experimentally (Fig. 2b). Quantifying the results, we find that if μ_{GS} is 10 D, as suggested above, then μ_{ES} is ~ 0 D.

Solvent-dependent TDCP signals for **1** with mixed configurations

TDCP signals for **1** in mixed solvents are considered a combination of responses from the ^3IL and ^3CT states. Fig. 3a presents the transients obtained for **1** measured in benzene mixed with CH_2Cl_2 . The signal amplitudes are normalized relative to absorbed laser energy to compare equal numbers of excited molecules. The TDCP response for **1** in 100% of CH_2Cl_2 is nearly identical to that of **3** in CH_2Cl_2 , implying similar ^3IL excited states for **1** and **3** in CH_2Cl_2 .^{3a} The volume percentage of CH_2Cl_2 was gradually decreased from 100% to 0% to tune the solvent polarity from systematically higher to lower. Across this series, the TDCP signal decreases with decreasing solvent polarity, from a large positive transient in 100% of CH_2Cl_2 to a slightly negative response in 0% CH_2Cl_2 (*i.e.* in pure benzene), consistent with the fact that the “pure” ^3IL character gradually changes to a mixed configuration with some ^3CT character. However, the polarity of benzene is not sufficiently apolar to shift the mixed configuration into one of “pure” ^3CT character.

The TDCP signal is expected to decrease more dramatically when benzene is replaced in the composition by *n*-hexane, a more non-polar solvent. This notion is indeed confirmed in Fig. 3b. The figure shows TDCP signals for **1** in *n*-hexane– CH_2Cl_2 mixtures (*v* : *v*) ranging from 60 : 40 to 0 : 100. Relative to CH_2Cl_2 in benzene, the transient amplitudes are markedly smaller for the same percentages of CH_2Cl_2 in *n*-hexane. Unfortunately, the solubility of **1** in *n*-hexane mixed with $<40\%$ of CH_2Cl_2 is insufficient for TDCP measurements. Nevertheless, extrapolation of the available experimental evidence leads to the expectation that the TDCP signal for $<40\%$ of CH_2Cl_2 would be negative in sign if it were measurable.

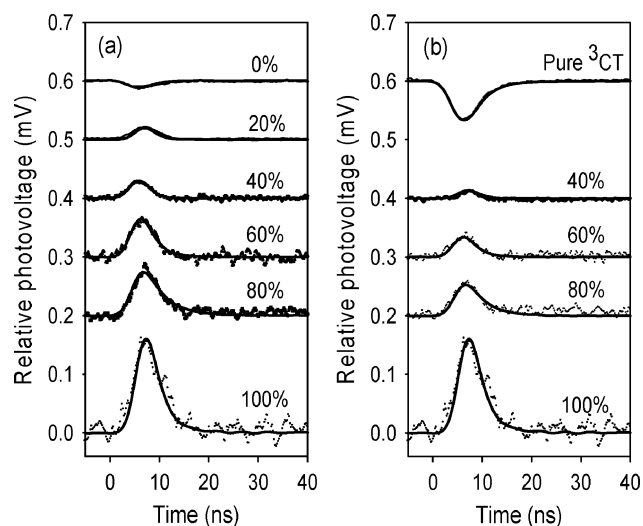


Fig. 3 TDCP signals for **1** in mixed solvents of CH_2Cl_2 and (a) benzene and (b) *n*-hexane with percentages of CH_2Cl_2 ranging from 0% to 100%. The signal in (b) for pure ^3CT is for **2** in CH_2Cl_2 .

Table 1 Fractions (x) of the ^3CT state in configuration mixing for compound **1** in solvent mixtures

% of CH_2Cl_2	x , fraction of the ^3CT state	
	In benzene	In n -hexane
0	0.24 ± 0.02	—
20	0.15 ± 0.02	—
40	0.13 ± 0.02	0.16 ± 0.02
60	0.10 ± 0.02	0.12 ± 0.02
80	0.05 ± 0.02	0.11 ± 0.02
100	0	0

By considering the limiting cases illustrated by compounds **2** and **3**, *i.e.* pure ^3CT and pure ^3IL excited states, we can use TDCP to quantify the extent of excited-state mixing occurring in **1** as a function of solvent composition. The quantification is approximate and includes the assumption that the amount (fraction, x) of ^3CT character is directly proportional to the amount of charge transferred. Similarly, we assume that the amount (fraction, $(1 - x)$) of ^3IL character is directly proportional to the extent of increase in molecular polarizability. Given these assumptions, the x -dependent TDCP signal will scale as:¹⁵

$$\text{Signal}(x) \propto \{(1 - x) \times \mu_{\text{GS}}\}^2 - \mu_{\text{GS}}^2 + (1 - x) \times C \times \Delta\alpha_{\text{V}} \quad (5)$$

where $C = 0.125$. C is the factor for converting polarizability volume (unit $\text{\AA}^3$) into the dipole moment squared (unit D^2). For better quantification, and to avoid any solvent effects contributing to values of μ_{GS} and $\Delta\alpha_{\text{V}}$, all the quantities in eqn (5) were measured in the same mixed solvent.

The fraction of ^3CT character present in photoexcited **1**, as estimated and described above, is summarized in Table 1. Note that the contribution is only 0.24 in pure benzene and that it decreases with increasing mole fraction of CH_2Cl_2 . This low ^3CT state contribution can be rationalized qualitatively by considering the relative energy levels of the pure ^3CT and ^3IL states measured in different solvents (Fig. 4). The ^3IL state is invariant to solvent composition whereas the ^3CT state lies 0.08 eV above the ^3IL state in benzene. Thus it is energetically more favorable for the ^3IL state to contribute in the configuration-mixed excited state. The ^3CT state lies only 0.03 eV below the ^3IL state in n -hexane, much less than the 0.16 eV gap between the ^3IL and ^3CT states in CH_2Cl_2 ;

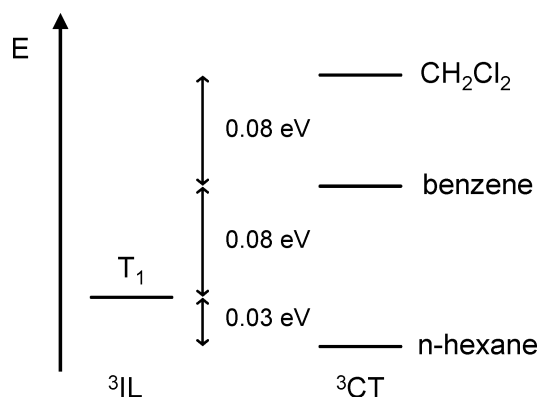


Fig. 4 Relative energy levels of the ^3IL and ^3CT states in n -hexane, benzene and CH_2Cl_2 . The ^3IL state is invariant in different solvents.

therefore, less than 0.5 ^3CT state character is expected in $>40\%$ CH_2Cl_2 . Greater ^3CT character in n -hexane + CH_2Cl_2 relative to benzene + CH_2Cl_2 , for a given percentage of CH_2Cl_2 , is also consistent with expectation from the relative energy levels presented in Fig. 4.

Conclusions

The excited state of $[\text{Pt}(\text{Bu}_2\text{bpy})(\text{PE}3)_2]$ (**1**) in mixed solvents with intermediate polarity was identified by transient absorption spectroscopy to be a configurationally mixed triplet state composed of ^3CT and ^3IL states. The transient absorption difference spectrum of the mixed triplet state is dramatically different from that of either the ^3CT -state model chromophore $[\text{Pt}(\text{Bu}_2\text{bpy})(\text{PE}1)_2]$ (**2**) or the ^3IL -state model chromophore $[\text{Pt}(\text{P}2)(\text{PE}3)_2]$ (**3**). The ^3CT , ^3IL and mixed triplet states were distinguished successfully by TDCP. The TDCP transients were negative in the case of ^3CT excited state in **2** and positive when the ^3IL state in **3** was produced. TDCP signals for **1** in mixed solvents are intermediate between those for the pure ^3IL and ^3CT states, with the magnitude dependent upon the polarity of the solvent. The fraction of ^3CT character in the configuration-mixed excited state was estimated by TDCP to be 0.24 in pure benzene, while it decreased to 0.05 in 20 : 80 benzene- CH_2Cl_2 . The fraction increased to 0.11 in 20 : 80 n -hexane- CH_2Cl_2 , reflecting the lower polarity of this solvent mixture.

Acknowledgements

CS and JTH thank the Weinberg College of Arts and Sciences, and the Basic Energy Sciences Program, Office of Science, US Department of Energy (DE-FG02-87ER13808) for financial support. AAR, XW, SG, AOE and FNC thank the Air Force Office of Scientific Research (FA 9550-05-1-0276) and the ACS-PRF (44138-AC3) for financial support.

Notes and references

- (a) C. J. Adams, N. Fey and J. A. Weinstein, *Inorg. Chem.*, 2006, **45**, 6105–6107; (b) C. J. Adams, S. L. James, X. Liu, P. R. Raithby and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 2000, 63–67; (c) F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro and N. Rajapakse, *Coord. Chem. Rev.*, 2006, **250**, 1819–1828; (d) C.-W. Chan, L.-K. Cheng and C.-M. Che, *Coord. Chem. Rev.*, 1994, **132**, 87–97; (e) S. Chan, W. Chan, Y. Wang, C. Che, K. Cheung and N. Zhu, *Chem.-Eur. J.*, 2001, **7**, 4180–4190; (f) E. O. Danilov, I. E. Pomestchenko, S. Kinayyigit, P. L. Gentili, M. Hissler, R. Ziessel and F. N. Castellano, *J. Phys. Chem. A*, 2005, **109**, 2465–2471; (g) F. Guo, W. Sun, Y. Liu and K. S. Schanze, *Inorg. Chem.*, 2005, **44**, 4055–4065; (h) F. Hua, S. Kinayyigit, J. R. Cable and F. N. Castellano, *Inorg. Chem.*, 2005, **44**, 471–473; (i) F. Hua, S. Kinayyigit, J. R. Cable and F. N. Castellano, *Inorg. Chem.*, 2006, **45**, 4304–4306; (j) W. Lu, M. C. W. Chan, N. Zhu, C.-m. Che, Z. He and K.-y. Wong, *Chem.-Eur. J.*, 2003, **9**, 6155–6166; (k) J. E. McGarrah and R. Eisenberg, *Inorg. Chem.*, 2003, **42**, 4355–4365; (l) I. E. Pomestchenko, C. R. Luman, M. Hissler, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2003, **42**, 1394–1396; (m) E. Shikhova, E. O. Danilov, S. Kinayyigit, I. E. Pomestchenko, A. D. Tregubov, F. Camerel, P. Retailleau, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2007, **46**, 3038–3048; (n) K. M.-C. Wong, W.-S. Tang, B. W.-K. Chu, N. Zhu and V. W.-W. Yam, *Organometallics*, 2004, **23**, 3459–3465; (o) V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong

- and K.-K. Cheung, *Organometallics*, 2001, **20**, 4476–4482; (p) C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, *Inorg. Chem.*, 2001, **40**, 4053–4062.
- 2 (a) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447–457; (b) I. E. Pomestchenko and F. N. Castellano, *J. Phys. Chem. A*, 2004, **108**, 3485–3492; (c) C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, *Inorg. Chem.*, 2001, **40**, 4053–4062.
 - 3 (a) S. Goeb, A. A. Rachford and F. N. Castellano, *Chem. Commun.*, 2008, 814–816; (b) A. A. Rachford, S. Goeb and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 2766–2767; (c) A. A. Rachford, S. Goeb, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2008, **47**, 4348–4355.
 - 4 (a) A. Harriman, M. Hissler, A. Khatyr and R. Ziessel, *Chem. Commun.*, 1999, 735–736; (b) K. Haskins-Glusac, I. Ghiviriga, K. A. Abboud and K. S. Schanze, *J. Phys. Chem. B*, 2004, **108**, 4969–4978; (c) Y. Liu, S. J. Jiang, K. Glusac, D. H. Powell, D. F. Anderson and K. S. Schanze, *J. Am. Chem. Soc.*, 2002, **124**, 12412–12413; (d) D. S. Tyson, J. Bialecki and F. N. Castellano, *Chem. Commun.*, 2000, 2355–2356; (e) D. S. Tyson and F. N. Castellano, *J. Phys. Chem. A*, 1999, **103**, 10955–10960.
 - 5 (a) H. Jude, J. A. K. Bauer and W. B. Connick, *Inorg. Chem.*, 2004, **43**, 725–733; (b) S. X. Liu and K. S. Schanze, *Chem. Commun.*, 2004, 1510–1511.
 - 6 (a) T. Ljungdahl, K. Pettersson, B. Albinsson and J. Martensson, *Eur. J. Org. Chem.*, 2006, 3087–3096; (b) E. A. Weiss, M. J. Ahrens, L. E. Sinks, M. A. Ratner and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2004, **126**, 9510–9511.
 - 7 (a) S. N. Smirnov and C. L. Braun, *Rev. Sci. Instrum.*, 1998, **69**, 2875–2887; (b) S. N. Smirnov and C. L. Braun, *J. Phys. Chem.*, 1992, **96**, 9587–9591.
 - 8 C. She, J. E. McGarrah, S. J. Lee, J. L. Goodman, S. T. Nguyen, J. A. G. Williams and J. T. Hupp, *J. Phys. Chem. A*, 2009, **113**, 8182–8186.
 - 9 (a) K. N. Grzeskowiak, S. N. Smirnov and C. L. Braun, *J. Phys. Chem.*, 1994, **98**, 5661–5664; (b) S. N. Smirnov and C. L. Braun, *J. Phys. Chem.*, 1994, **98**, 1953–1961.
 - 10 $\Delta\alpha_V = \Delta\alpha/4\pi\epsilon_0$, where ϵ_0 is the vacuum permittivity.
 - 11 S. N. Smirnov and C. L. Braun, *Chem. Phys. Lett.*, 1994, **217**, 167–172.
 - 12 (a) F. W. M. Vanhelmont and J. T. Hupp, *Inorg. Chem.*, 2000, **39**, 1817–1819; (b) F. W. M. Vanhelmont, R. C. Johnson and J. T. Hupp, *Inorg. Chem.*, 2000, **39**, 1814–1816.
 - 13 Y. J. Kang, J. Lee, D. T. Song and S. N. Wang, *Dalton Trans.*, 2003, 3493–3499.
 - 14 J. E. McGarrah, J. T. Hupp and S. N. Smirnov, *J. Phys. Chem. A*, 2009, **113**, 6430–6436.
 - 15 The more precise expression is: $\text{Signal}(x) \propto \{[(1-x)\mu_{\text{GS}}]^2 - \mu_{\text{GS}}^2\} + C \times [(1-x) \times \alpha_{\text{GS}} - \alpha_{\text{GS}}]$. α_{GS} is calculated to be $37 \text{ \AA}^3$ for $(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_3\text{H}$ using HyperChem Pro 6.0. α_{GS} is small enough to validate eqn (5) for simplified calculations. Also contributing to the simplicity of eqn (5) is the assumption (see text) that $\mu_{\text{ES}} \approx 0 \text{ D}$.