

Time-resolved resonance Raman spectroscopy and isotopic substitution: probing the structure of charge-separated excited state in Pt(II) diimine (bis)thiolates

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This contribution reports *ps* TR³ studies into the structure of the charge-separated excited state in metal thiolates.

Introduction

Photo-induced electron transfer is one of the elementary processes, which is utilized in many natural or man-made applications of light energy conversion, such as photosynthesis or photocatalysis¹. In these processes, a Donor-Spacer-Acceptor (D-sp-A) unit is the component responsible for the photo-induced-electron transfer step, with a charge-separated excited state, [D⁺-sp-A⁻]*, as a key transient¹. However, the reactivity of this state is largely dependent on the thermodynamically favourable back electron transfer that regenerates the ground state. A key challenge is to control back electron transfer in a rational manner. We are developing *structural reorganisation in the excited state*, namely formation of a transient sulfur-sulfur three-electron bond, S[·]:S[·], on a metal template, as a tool to control back electron transfer.

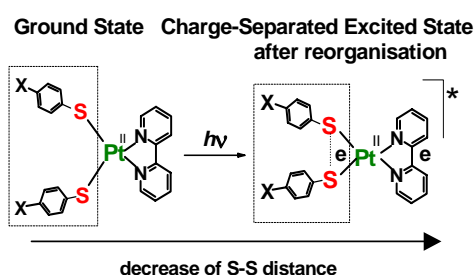


Figure 1. Suggested formation of a three-electron sulfur-sulfur bond with a concomitant shortening of the sulfur-sulfur distance in the excited state of metal thiolates.

The Pt(II) diimine (bis)thiolates, (NN)Pt(SR)₂, have acted as model compounds in our studies, since the HOMO in these compounds has thiolate/Pt(d) origin, while the LUMO is predominantly localised on the diimine ligand. In these systems (Figure 1), light induces electron transfer from the thiolate moiety to the diimine³⁻⁵, forming a thiolate anion and thiyl radical, which can interact with each other via the metal centre. These systems are therefore suitable for formation of a transient S-S bond in the excited state. The formation of a new bond in the excited state, which is not present in the ground state, creates an activation barrier for back electron transfer, thus giving one a tool to control the rate of this process.

The formation of a transient S[·]:S[·] bond have been probed so far by the studies of dynamics and photoreactivity of the lowest excited state in the diimine (bis)thiolates as a function of thiolate ligand, and by quantum-chemical calculations⁶:

(I) Studies on excited state dynamics and on photoreactivity as a function of thiolate showed that changes in the thiolate structure and donor capability allows one to vary the lifetime from 9 to 840 ps; and photooxidation quantum yield from 10⁻³ to 0.1. The trend in photoreactivity and lifetimes correlates

directly with the estimated energy of the transient S[·]:S[·] bond (32 to 6 kcal/Mol)⁶.

(II) The quantum-chemical calculations (HF/6-31G*) have shown that the HOMO of the triplet state of the model system is a singly-occupied antibonding, and HOMO-1 – doubly-occupied bonding combination of p-orbitals of the two S atoms, suggesting a presence of a S-S bond in this excited state⁷. The results summarized above provided significant indirect support of the presence of S[·]:S[·] bonding in the lowest triplet charge-separated excited state of model chromophores. This contribution is concerned with the preliminary studies onto the structure of this excited state.

Results and discussion

Time-resolved resonance Raman (TR³) is an excellent method for obtaining direct structural information on the excited states of metal chromophores⁸. Since $\nu(SS)$ is strongly Raman active, the picosecond TR³ provides a *direct* route to probe the sulfur-sulfur interaction in the excited state of Pt(NN)(RS)₂. For disulfides RSSR, the $\nu(SS)$ energy is strongly dependent on “R”, ranging from 550 to 450 cm⁻¹. Due to a single-occupied antibonding character of the HOMO in the S[·]:S[·] species⁹, and an anticipated Pt(II) contribution, one could expect $\nu(SS)$ vibration in our systems to occur in the region below 500 cm⁻¹.

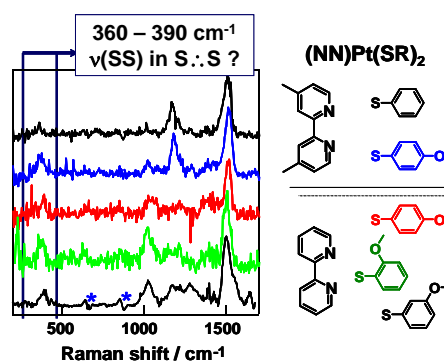


Figure 2.¹² The TR³ spectra of model compounds previously obtained under 400 nm pump / 500 nm probe configuration. * Non-compensated solvent absorptions. Please note the differences in (i) the data obtained for the compounds containing 4,4'-diMe-2,2'-bpy (top) and 2,2'-bpy (bottom); and (ii) the relative intensities of the 390 cm⁻¹ and ca. 1500 cm⁻¹ band.

The TR³ experiments were performed for the (NN)Pt(RS)₂, presented on Figure 2, right. The excited state was generated by 400 nm pump pulse (150 fs), and then probed by 400, 450, 488, 500 and 780 nm pulse at different time delays. Under 500 nm probing performed previously¹², the compounds studied all show the similar Raman pattern (Figure 2, left) featuring the vibration at ca. 390 cm⁻¹, where $\nu(SS)$ can be anticipated. No Raman signal was detected for Pt(bpy)(PhSe)₂, Pt(bpy)(4-MeO-PhO)₂, and Pt(bpy)Cl₂, in

which the lowest excited state retains {charge-transfer to bpy} nature, but is not suitable for S...S interaction¹². So far, the assignment of individual vibrations in the TR³ spectra obtained remains ambiguous for a number of reasons:

- (i) The $\nu(\text{SS})$ vibration will only be resonantly enhanced if the probing wavelength in TR³ is in resonance with the transition involving either bonding, or anti-bonding S-S orbitals;
- (ii) The Raman vibrations of NN and RS ligands overlap across the whole spectral region. E.g., bpy-anion has characteristic Raman bands¹⁰ at 1558, 1497, 1205, 1151, 1033, 986, 740, 660, 370 cm⁻¹, and PhS-radical¹¹ - at 1551, 1180, 1073, 724 cm⁻¹.

The region below 500 cm⁻¹ is of particular interest as that is where $\nu(\text{SS})$ can be anticipated. However, it is also characteristic for $\nu(\text{Pt-S})$, $\nu(\text{Pt-N})$ and some intra-ligand modes. We have given a review of the literature data on possible assignments of these vibrations previously¹²; various bands in the region 140 – 405 cm⁻¹ have been assigned to $\nu(\text{Pt-S})/\nu(\text{Pt-N})$ but no definitive assignment for Pt(NN)(thiolate) has been made. In the Raman spectrum of [Fe^{II}(bpy)₃]²⁺, the vibration at 370 cm⁻¹ was assigned to bpy, to bpy⁻ for [Fe^{II}(bpy)₂(bpy⁻)]⁺, and to intra-phenanthroline (phen) mode for [Fe^{II}(phen)₃]²⁺¹³. It therefore seems possible that the band at 390 cm⁻¹ observed in Raman spectra of the charge-transfer excited state of the model chromophores (Figure 2) is due to an intra-ligand vibration of a coordinated bpy-radical anion.

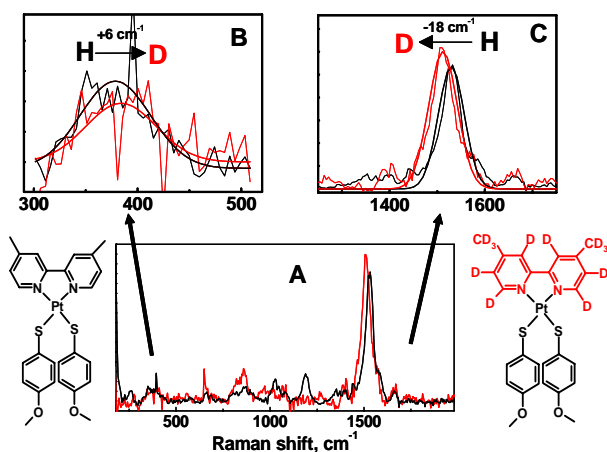


Figure 3. (A) TR³ spectra of Pt(4,4'-diMe-2,2'-bpy)(4-MeOPhS)₂ and its d₁₂-diMe-bpy analogue, in DMF, 400 nm pump, 450 nm probe, 10 ps delay. While a -18 cm⁻¹ shift observed for the ca. 1510 cm⁻¹ band clearly indicates that corresponding vibration is localised on the bpy-anion, the shift for the “390” band is slightly positive. (B) The Gauss parameters for the low frequency band are: h₁₂; $\nu(\text{max})$ 379±3 cm⁻¹, FWHM 68±10 cm⁻¹; d₁₂ 384±6 cm⁻¹, 68±18 cm⁻¹. (C) The Gauss parameters for the high frequency band are: h₁₂; $\nu(\text{max})$ 1529±1 cm⁻¹, FWHM 54±2 cm⁻¹; d₁₂: 1512±1 cm⁻¹; 60±2 cm⁻¹.

The present contribution explores isotopic substitution and Raman excitation profiles to help with the assignment of the vibrational signature of the excited state.

(A) Isotopic substitution.

Ideally, ³²S/³⁴S isotopic substitution should have been used. However, the effect expected would be rather small, and taking into account the spectral resolution (ca. 4 cm⁻¹) and the S/N ratio (Figure 2), these experiments were not performed. Instead, deuteration of the diimine ligand has been used as a

way to probe whether “390” band is due to bpy-radical anion. To the best of our knowledge, the only data reported in the literature with respect to isotopic effect on the low frequency modes of bpy radical anions are those for [Pt(bpy)₂][ClO₄]₂, where upon deuteration of the bpy-ligand a negative shift of -15 cm⁻¹ has been observed for 370 cm⁻¹ vibration¹⁴. The following conclusions can be drawn from the TR³/isotopic substitution data presented in Figures 3 and 4:

- (i) The pronounced negative shift of the high frequency band, at ca. 1500 cm⁻¹, upon deuteration indicates that the corresponding vibration is localised on the bpy-radical anion formed in the excited state. The isotopic shift observed is the same for 4,4'-diMe-2,2'-bpy (Figure 3) and 2,2'-bpy (Figure 4).
- (ii) The “390” band. Slight negative (-7 cm⁻¹) shift of this vibration was observed upon deuteration of the bpy ligand (Figure 4), while most surprisingly +6 cm⁻¹ shift was detected for this vibration for the d₁₂-Mebpy-Pt(4-MeOPhS)₂ compound vs. its h₁₂ analogue. Thus, the deuteration of the diimine ligand has not, unfortunately, supplied evidence either for or against localisation of the “390” vibration on the diimine radical anion.

Several other observations are *not* in line with an assignment of “390” band to the diimine radical anion:

- (i) In the Raman spectrum of [Fe^{II}(bpy)₂(bpy⁻)]⁺ (501.78 nm)¹⁰ the band at 370 cm⁻¹ of bpy⁻, is accompanied by a 30 % weaker band at 519 cm⁻¹, and a 50 % weaker band at 740 cm⁻¹. Although the S/N ratio should allow us to detect these vibrations, they are not seen in the spectra obtained (Figure 2).
- (ii) The intensity ratio between the “390” band and the high-frequency bands depends on both diimine and thiolate ligand (Figure 2). Should the 390 cm⁻¹ vibration be localised on bpy⁻, the ratio of these intensities would be independent on the structure of the compound under the same probing wavelength.

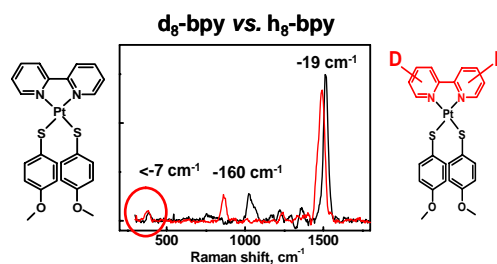


Figure 4. TR³ spectra of Pt(2,2'-bpy)(4-MeOPhS)₂ and its d₈-bpy analog, in DMF, 400 nm pump, 488 nm probe. While a -19 cm⁻¹ shift observed for the ca. 1510 cm⁻¹ band clearly indicates that corresponding vibration is localised on the bpy-anion, the shift for the “390” band is <-7 cm⁻¹, which is within experimental error.

(B) Raman excitation profile

As has been mentioned above, the $\nu(\text{SS})$ vibration will only be resonantly enhanced if the probing wavelength in TR³ is in resonance with the transition localised on either bonding, or anti-bonding S-S orbitals. The excitation profile experiments have been attempted, in order to start identifying the electronic transitions of the excited state which would involve S...S-bonding, and the vibration localised on the S...S bond.

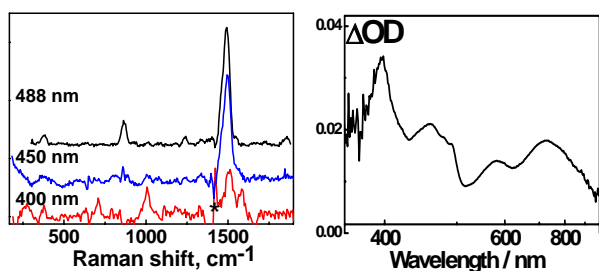


Figure 5. Left: TR³ spectra of Pt(d₈-2,2'-bpy)(4-MeOPhS)₂ in DMF, 400 nm pump, 10 ps delay. Right: TA spectrum¹⁵.

The preliminary results for Pt(d₈-bpy)(4-MeOPhS)₂ under 400, 450 and 488 nm probe are shown on Figure 5 (left).

- (i) All 3 absorption bands investigated seem to be due to transitions at least partly localised on the bpy-moiety as is indicated by the intense band at ca. 1510 cm⁻¹, present in all the spectra, which (see above) has shown a strong isotopic effect.
- (ii) New 1590, 1010 and 700 cm⁻¹ bands are emerging in the Raman spectrum on moving from 488 to 400 nm probing wavelength; while the 860 cm⁻¹ band disappears. These observations suggest that 400 and 500 nm electronic transitions of the excited state are at least partly localised on the different parts of the bpy-radical anion moiety. This also suggests that 450 nm absorption band is an overlap of at least two electronic transitions.
- (iii) It is somewhat difficult to make a judgement with respect to the origin of the “390” vibration on the basis of the excitation profile results obtained: this vibration is present upon probing at 488, 450, and 400 nm. However, the ratio between the intensity of this band and the one which is bpy-localised, is larger for the 488 nm probing wavelength than for the 450 nm one. (The ca. 270 cm⁻¹ vibration observed in the Raman spectrum under 400 nm probe could be due to an over subtraction at the very edge of the laser line; further data analysis is required to check the reliability of this band).

The experiments have been attempted to identify the nature of the 780-800 nm absorption band observed in the excited state. The position of this band is both diimine and thiolate ligand dependent (Figure 5 right)¹⁵, and it thus could be anticipated that this band is due to a charge-transfer transition in the lowest excited state. However, no TR³ signal was observed for several Pt(II) diimine thiolates under the conditions otherwise identical to the 400-500 nm experiments.

Summary

The absorption spectra of the lowest excited state of (NN)Pt(SR)₂, which could reorganize with a formation of a transient S^{·-}:S bond, clearly suggest an overlap of several electronic transitions in the region 400 - 500 nm. The difference between the Raman pattern observed in resonance with the 400, 450 and 488 nm electronic transitions of the lowest excited state and the one expected for bpy-radical anion suggests that all of these absorption bands result from an overlap of at least two electronic transitions. The gradual change of the Raman profile on going from 400 to 500 nm excitation suggests that the electronic transitions which make major contribution to these absorption bands, are localised, at least partly, on different parts of the bpy-radical anion moiety.

The Raman band has been detected for the lowest excited state of (NN)Pt(SR)₂ at ca. 390 cm⁻¹, in the region where ν(S^{·-}:S) could be anticipated. However, Pt-S, Pt-N and intra-bpy

vibrations could also signal in this spectral region. The lack of other low-frequency bands associated with this one in the spectrum of bpy-anion¹³, and the dependence of the relative intensities of the Raman vibrations observed on the structure of the compounds makes the assignment of the “390” band to bpy-anion less likely. The absence of Raman data for Pt(bpy)(PhSe)₂, Pt(bpy)(4-MeO-PhO)₂, and Pt(bpy)Cl₂, under identical experimental conditions does *not* support either ν(Pt-N) or intra-bpy⁻ assignments of the band at 390 cm⁻¹.

The very small shift observed for the 390 cm⁻¹ band upon deuteration of the diimine ligand neither proves, nor eliminates, the preliminary assignment of this band to the transient S^{·-}:S bond, but indicates that it is unlikely for this vibration to be localised on the bipyridine moiety.

The negative shift observed for the 1500 cm⁻¹ vibration upon deuteration of the diimine ligand suggests that this vibration is due to diimine ligand radical anion.

At present, no Raman data are available for disulfide radical anions, neither for ground state radical anions of Pt(II) diimine chlorides and thiolates. We are currently working on (spectro)electrochemistry Raman / isotopic substitution experiments in order to obtain these data which could prove essential for the assignment of the vibrational signatures of the charge separated excited states in model chromophores.

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Experimental arrangements

The picosecond TR³ experiments on the Kerr gate apparatus¹⁶ were performed in DMF, under vertically flowing open jet sample arrangement. The 400 nm pump and 500 nm probe wavelengths were used, with typical pulse energies ca. 10 μJ (pump) and 3 μJ (probe), and both beam diameters being ca. 150 μm at the sample. Acetonitrile Raman bands were used for calibration the spectra, with an estimated accuracy of the absolute frequency ± 10 cm⁻¹. Approximately 1000 s integration time was used for each time delay. All the TR³ spectra were first corrected for the solvent absorptions by the scaled subtraction of the solvent spectrum. The pure excited spectra were then obtained by a scaled subtraction of the spectrum at a negative time delay from the spectrum at the time delay of interest.

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