Quadruple Electron Storage using Visible Light with Nitrogen-Heterocycles under Metal-Free

Conditions

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Abstract: A byproduct of the synthesis of 9,11,20,22-tetra-aza-tetrapyrido[3,2-a:2'3'-c:3'',2''-l:2''',3''']-pentacene (tatpp) is the symmetrical dimer ditatpp, which is linked by a carbon-carbon bond along the central benzene ring. The structure of the dimer has been determined by X-ray crystallography and reveals a dihedral angle of 73° between the two tatpp units, which is likely due lone pair repulsion on the adjacent aza nitrogens on each tatpp unit. Because of this non-planar geometry, this ditatpp dimer is freely soluble in organic solvents, such as ethanol, very much unlike the tatpp ligand, which is sparingly soluble in all common solvents. Photolysis of ditatpp with visible light in the presence of sacrificial donors, such as triethylamine, results in multi-electron reduction on each of the tatpp units, as determined by absorption spectroscopy. As the tatpp units appear to function independently of one another, and each tatpp unit is reduced by two electrons and is doubly protonated in the final compound, the photoreduction results in a net storage of 4 electrons in the fully reduced species.

Introduction

Photocatalysts capable of multi-electron storage are of particular interest, given the multi-electron nature of most fuel forming reactions.¹⁻⁴ Historically, the majority of photo-catalysts developed for this purpose utilize precious metals, such as Ru, Re, and Pt, which are scarce and expensive.^{3,5-16} As an alternative to using expensive transition metals, organic nitrogen-heterocycle chromophores, such as phenazine (phz) or dipyridophenazine (dppz), have also been shown to store multiple electrons upon photoreduction, however these chromophores typically absorb in the UV region of the spectrum.^{5,17,18} Ferraudi and coworkers¹⁹ describe the photoexcitation processes for these chromophores as occurring via a low-lying ³(π - π^*) state, which can undergo reductive quenching in the presence of sacrificial donors such as triethylamine (TEA) and triethanolamine (TEOA) to yield the radical species dppz[•] or phz[•]. Protonation of the resulting dppz[•] or phz[•] radicals results in disproportionation, yielding the doubly-reduced, doubly-protonated products dppzH₂ or phzH₂ and starting material, dppz or phz.^{5,18} The

photoreduction is readily followed by appearance of a characteristic broad peak in the visible region at 400 - 550 nm and is associated with the doubly-reduced, doubly protonated compounds dppzH₂ or phzH₂. The related tatpp nitrogen-heterocycle shows similar photochemistry with Guo and Obare reporting the two electron photoreduction to H₂tatpp in DMSO in the presence of TEA.²⁰ Like dppz and phz, tatpp double reduction and protonation is accompanied by a broad new absorption growing in at 560 nm (DMSO, $\epsilon = 6500 \text{ M}^{-1}\text{cm}^{-1}$). Importantly, the tatpp ligand, with its extended aromatic system, is a visible light chromophore, with two strong sharp peaks at 435 and 460 nm. Unfortunately, the sparing solubility of tatpp limits its study to dilute DMSO solutions, unless excess Zn(II) is added upon which the Zn-tatpp-Zn adducts exhibit decent solubility in alcohols and MeCN.^{21,22}

We had previously shown that the tatpp ligand in [Ru(phen)₂tatppRu(phen)₂]⁴⁺ (**P**⁴⁺) acts as a two-electron, two proton storage reservoir upon visible light irradiation of **P**⁴⁺ in water or MeCN in the presence of TEOA or TEA.^{14,16,23} Unlike the pure organic system, the second reduction may also be driven photochemically if the system pH is insufficient to protonate the radical intermediate **P**^{3+•}.^{23,24} While the photochemistry of this compound is primarily thought to involve ³MLCT excited states, a ³tatpp state is part of the excited state manifold, and is energetically near the lowest lying ³MLCT state.^{25,26} As shown in Figure 1, the reductions are localized on the tatpp ligand and occur in a stepwise fashion. The identity of **P**^{3+•}, the doubly-reduced, singly-protonated **HP**³⁺, and doubly-reduced, doubly-protonated H₂**P**⁴⁺ were all confirmed by following the spectral changes observed upon chemical titrations with cobaltocene and trifluoroacetic acid and with complementary spectroelectrochemical techniques. The most prominent spectral features for the radical **P**^{3+•} being the appearance of a structured peak near 900 nm and for H₂**P**⁴⁺ a new broad band at 560 nm.

During large scale preparations of tatpp we discovered that dimer formation occurs, where tatpp monomer units are linked by a carbon-carbon bond between the central benzene unit of each ligand. Ditatpp formation is a minor side product, and demonstrates excellent solubility in common organic solvents. Because of lone pair repulsions, the two π -systems are nearly orthogonal to each other and thus, the tatpp subunits appear to act independently. In this work, we describe synthesis, characterization, and photochemistry of this soluble dimer, ditatpp, and demonstrate that visible-light photolysis of this compound leads to a four-electron reduction of the compound. The process can be

reversed upon exposure to air, the ditatpp is reformed. Ditatpp is used to prepare the fully ruthenated tetramer, $[(\text{Ru}(\text{phen})_2)_4(\text{ditatpp})](\text{PF}_6)_8$, which, while formed, is difficult to purify beyond 90% purity.

Materials and Methods

1,2,4,5-benzenetetramine tetrahydrochloride (BTA) (Sigma Aldrich, CAS: 4506-66-5) was purified according to literature procedures.²⁷ 1,10-Phenanthroline-5,6-dione (phendione) was synthesized and purified according to literature procedures.^{13,28} All reactions were performed under aerobic conditions unless otherwise specified. All solvents were used without further purification.

Synthesis of tatpp and ditatpp

The standard preparation of tatpp according to literature procedures,^{13,28} was modified as described. BTA (2.0 g, 7.0 mmol) was added to a 200 mL round bottom flask with 4.5 g phendione (21.4 mmol), and 125 mL of dry ethanol. This solution was refluxed under N_2 for 6 days without K_2CO_3 , which is usually present during tatpp preparation.¹³ The slurry was filtered with a medium porosity fritted funnel and the filter cake was washed with hot ethanol until no color eluted from solvent washings. The cake contains the crude tatpp whereas the filtrate contains the dimer ditatpp.

Isolation of tatpp: The filter cake was washed with 100 mL acetone, and transferred to a large beaker in which the solid was mulled with 16 g $\text{Zn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ until a uniform paste had formed, after which 500 mL MeCN plus 10 mL H_2O was added. The solution was heated to reflux with constant stirring and the resulting solution filtered hot to remove undissolved solids. After cooling, 150 mL of 3 M NaOH was added to the solution and stirred for 1 h, during which a dark solid precipitated from solution. The solution was filtered, and the precipitate washed with copious amounts of hot DI water. The filter cake was then washed with hot ethanol (50 mL), and a 1:1 mixture of dichloromethane/chloroform (3 x 100 mL), with special attention made to save all filtrate washings for use in isolation of ditatpp. A second wash was performed on the solid, using hot water (100 mL), ethanol (100 mL), dichloromethane (100 mL), and then dried in vacuo at 50° C for 24 hr, to afford 1.4 g tatpp (70% yield). ^1H NMR (500 MHz) was obtained

in MeCN- d_3 upon addition of an excess $\text{Zn}(\text{BF}_4)_2$ hydrate: δ = 9.93 (d, J = 13.75 Hz, 4 H), 9.58 (s, 2 H), 9.25 (d, J = 8, 4 H), 8.32-8.28 (dd, J_1 = 13.15, J_2 = 5, 4H) ppm.

Isolation of ditatpp: The initial filtrate, plus the ethanol and 1:1 dichloromethane/chloroform washings were combined, and the solvent was removed under reduced pressure. The solids were re-dissolved in a minimal amount of ethanol (~5 mL), and then precipitated by slow addition of up to 100 mL acetone. The solid obtained was filtered with a 0.2 μm nylon membrane, then re-dissolved in a minimal amount of dichloromethane (~5 mL). The solution was then passed through a glass wool plug in a disposable pipette to remove undissolved solids. Upon allowing the dichloromethane solution to evaporate, a dark red solid precipitated, which was isolated by filtration using a 0.2 μm nylon membrane. The solid was washed with 10 mL 90:10 acetone/ethanol, then dried in a vacuo at 50° C for 24 hr, to yield the ditatpp, 55 mg (0.73% yield). ^1H NMR (500 MHz, CDCl_3 - d_1): δ = 9.95 (s, 2 H), 9.87 (d, J = 9.6, 4 H), 9.26 (d, J = 6.2 Hz, 4 H), 8.93 (d, J = 6.5 Hz, 4 H), 8.21 (d, J = 9.6 Hz, 4 H), 7.89 (dd, J = 12.7 Hz and 3.8 Hz, 4 H), 7.17 (dd, J = 12.7 Hz and 3.4 Hz, 4H) ppm. MALDI-TOF: $[(\text{M} + 2 \text{Na}^+)]^+$: calc: 1016.9 m/z, found: 1017.6 m/z. X-ray quality crystals were grown by layering toluene on CH_2Cl_2 solution (1:3) of ditatpp.

Synthesis of $[(\text{Ru}(\text{phen})_2)_4(\text{ditatpp})](\text{PF}_6)_8$

Ditatpp (90.0 mg, 92.8 μmol) was added to freshly prepared $[\text{Ru}(\text{phen})_2]\text{Cl}_2$ (230 mg, 432 μmol , 4.6 equiv)²⁹ in 100 mL of EtOH under N_2 , and refluxed for 48 hours. The solution was cooled, filtered with a 0.2 μm nylon membrane, and 100 mL H_2O was added to the filtrate. NH_4PF_6 was added in excess to precipitate a nearly black solid which was filtered with a 0.2 μm nylon membrane and dried in a vacuo at 50 °C for 24 hr. The product was purified by double metathesis: First the crude product was dissolved in acetone (20 mL), filtered, and the chloride salt precipitated by dropwise addition of a saturated acetone solution of tetrabutylammonium chloride (Bu^n_4NCl). The resulting precipitate was filtered, washed with fresh acetone, and dried at 50 °C for 24 hr. The nearly black solid was then dissolved in 20 mL D.I. H_2O , filtered, and dropwise addition of a saturated aqueous ammonium hexafluorophosphate solution resulted in the precipitation of the hexafluorophosphate salt. The precipitate was filtered, washed with water and then diethyl ether and dried in a vacuo at 50 °C for 24 hr. This process was repeated two more times to afford $[(\text{Ru}(\text{phen})_2)_4(\text{ditatpp})](\text{PF}_6)_8$ 325 mg (86 % yield). $^1\text{HNMR}$ (500 MHz, MeCN- d_3): δ = 10.07 (s, 2 H),

9.75-9.67 (m, 5 H), 8.6-7.08 (m, 134 H) ppm. ESI-MS: (M - 3 PF₆)³⁺, (M - 4 PF₆)⁴⁺, (M - 5 PF₆)⁵⁺, (M - 6 PF₆)⁶⁺, (M - 7 PF₆)⁷⁺, (M - 8 PF₆)⁸⁺ calc: 1181.67, 850.07, 651.73, 518.47, 423.73 m/z found: 1181.67, 850.07, 651.73, 518.47, 423.73, 352.67 m/z.

X-ray Crystallography: The solvent system was highly volatile therefore, the crystals were acutely air-sensitive. Crystals began to de-solvate only seconds after removing from the mother liquor and mounting of the crystals was executed hastily. Crystals were drawn out of their vials using a pipette, and placed onto a glass slide previously stored in a freezer. The crystals themselves were visibly twinned and time did not allow proper removal of twinned crystals by cutting. A large twinned crystal was mounted onto a cyro-loop and data was collect under cold nitrogen flow at 100 K. A unit cell determination failed because of the twinning problem, however the data was de-twinned using the software Cell_Now provided by Bruker-AXS.³⁰ A reasonable cell was selected by calculating the volume of the putative structure and data was collected for a period of 18 hours. The complete data set was processed using the SAINT (version 6.45) and TWINABS software provided by Bruker-AXS.³⁰ An hklf4 and hklf5 reflection file was generated and the hklf4 file was used to solve the structure. Later, towards the end of the refinement, the hklf5 reflection file was used to finalize the refinement. The non-hydrogen atoms are refined anisotropically and hydrogen atoms were added in calculated positions. Co-crystalized toluene and dichloromethane molecules were found in the unit cell. The disorder of the solvent molecules were solved with a combination of restraints: dfix, dang and anisotropic parameters. The final agreement factors are admittedly high but attempts to recollect on a better quality crystal were unsuccessful due to the highly volatile nature of the samples. However, the spacegroup and structure are unambiguous and clearly show evidence of a dimeric structure and the dihedral angle is well determined. Full crystallographic details and tables containing bond distances and angles are located in Supporting Information.

Photochemistry: A stock solution of ditatpp was prepared by diluting 1.27 mg of material in a 50.00 mL volumetric flask with 100% EtOH. Aliquots (3.0 mL) of the stock solution were transferred to freshly cleaned quartz cuvettes (b = 1 cm) which were fitted with a screw cap and septum seal. Prior to addition of TEA, the solution was de-gassed with N₂, and the initial UV/Vis spectra was obtained using a Hewlett Packard 8453 UV-Visible Spectrophotometer. While continually de-gassing the solution, 0.1 mL TEA was

added slowly. Samples were then irradiated using a custom light source ($\lambda_{\text{max}} = 470 \text{ nm}$) previously described in the literature.^{24,31} Chemical actinometry using potassium ferrioxalate³² gave an average photon flux of $36 \times 10^{-3} \text{ Einstein h}^{-1}$. After photolysis was complete, samples were exposed to O_2 by using a pipette to bubble air through the solution which was then allowed to rest 5 minutes prior to final spectral analyses.

Results and Discussion

The ditatpp dimer is a minor byproduct formed during the preparation of the free tatpp ligand and is only isolated in less than 1 % yield. Unlike tatpp, the dimer ditatpp is freely soluble in numerous organic solvents and was only discovered by chance, as the common purification procedure for tatpp involved extensive washings which were typically discarded. While the exact mechanism of formation is unclear, it seems reasonable that tatpp in solution may be reduced by some benzene-tetrammine to form a radical species that couples at the bridgehead position, and is then re-aromatized upon oxidation by reaction with phenidone. Reaction run under aerobic conditions did not yield any ditatpp but gave similar yields of tatpp.

The ^1H NMR of the tatpp and ditatpp are shown in Figure 2. All of the hydrogens are attached to aromatic rings and, as expected, found in the downfield aromatic region. Both molecules have D_{2h} point group symmetry however, the dimer has 7 unique hydrogens and while the monomer only has 4. This is clearly observed in the NMR spectrum with tatpp showing a single AMX coupled set for H_a , H_b , and H_c plus the singlet for the central H_d . The dimer ditatpp has an inner AMX coupled set (H_f , H_g , H_h) and outer A'M'X' coupled set (H_a , H_b , and H_c) plus the central H_d singlet. Integration shows that the ratio of H_d to H_a (or any of the other hydrogens) of 1:2 for tatpp and ditatpp as expected. Due to the poor solubility of tatpp, its spectrum required addition of an excess of $\text{Zn}(\text{BF}_4)_2$ to solubilize the ligand in MeCN-d_3 , while the ditatpp dimer was freely soluble in CDCl_3 . Unfortunately, this solvent change makes direct comparisons of the chemical shifts relatively meaningless as large shifts are observed upon changing solvents. It suffices to say, the NMR are completely compatible with the proposed structures.

Single crystal X-ray crystallography of the ditatpp crystal showed that it crystallized in a triclinic system with a $P\bar{1}$ space group. This structure shows a ditatpp molecule co-crystallized with six dichloromethane and five toluene solvent molecules in the asymmetric unit. As seen in Figure 3, the

dimeric structure is readily apparent and the central C-C bond distance of 1.496 Å, which is very similar to the related C-C bond distance reported for an anthracene dimer.³³ The dihedral angle of the planar aromatic units about the C-C bond in ditatpp is 73°, whereas the same angle for the anthracene dimer is 80°. The increased twisting in tatpp indicates that the aza nitrogen lone pair repulsion is not as strong a steric restraint as having hydrogens in these locations. While the dihedral angle in the crystal structure is fixed, in solution the average dihedral angle averages 90° as there is freedom to expand the dihedral angle but not to compress it. At 90°, the two orthogonal π systems will have zero electronic overlap, suggesting that the two chromophore units will largely behave independently.

The $[(\text{Ru}(\text{phen})_2)_4(\text{ditatpp})](\text{PF}_6)_8$ complex was prepared by reaction of the free ditatpp ligand with a slight excess of $\text{Ru}(\text{phen})_2\text{Cl}_2$ in refluxing ethanol. The complex was purified by repeated metathesis between the chloride and hexafluorophosphate salt. The final product shows the parent peaks in the ESI-MS, and the ^1H NMR spectrum, shown in Figure 4, reveals a number of new peaks that would at first appear to be impurities, as indicated by the asterisks. However, careful analysis of the downfield region indicates that some, if not all of these peaks are due to the stereochemical heterogeneity of the product. Each metal center can exist in either the Λ or Δ stereochemical configuration giving rise to a 2^n ($n=4$) mixture of enantiomers and diastereomers, the latter of which could be expected to have different chemical shifts between diastereomers. Previous studies on tatpp dimers as well as dimers with shorter tetrapyridophenazine (tpphz) ligands have shown that the stereochemical isomerism is not detectable in simple linear dimers, as the stereocenters are anywhere from 12 Å (in tpphz dimers) to 17 Å (in tatpp dimers) and cannot approach any closer.³⁴⁻³⁸ This is not exactly the case with the tetramer in which stereocenters on the same tatpp portion are still spatially separated, however, stereocenters on adjacent tatpp units can and do interact. This is most readily observed in the downfield doublets at 9.66, 9.70, and 9.74 ppm, which are present in a 2:4:2 ratio. If the inner H_e and outer H_c hydrogens were magnetically equivalent, only two doublets of equal intensity should be observed. The H_d singlet at 10.1 ppm reveals that for this position, the metal stereochemistry is irrelevant, however the adjacent three doublets can only be explained if we obtain different chemical shifts for cases in which adjacent centers are homochiral ($\Delta\Delta$ or $\Lambda\Lambda$) or heterochiral ($\Delta\Lambda$ or $\Lambda\Delta$). As these are expected to be present in a 1:1 ratio, the H_e peak is now observed as a doublet at either 9.66 or 9.74 ppm whereas the outer H_c is seen at 9.70 regardless of the

stereochemistry. The chemical shifts between diastereomers differ the greatest for the H_e, H_f and H_g tatpp hydrogens, as well as the hydrogens on the phenanthrolines on the inner-side of the complex. Conversely, the H_a, H_b, and H_c are the least affected, being the furthest spatially from the site of where the two stereocenters interact.

The absorption spectrum of the free ditatpp dimer in ethanol and the associated changes upon irradiation with visible light in the presence of TEA are shown in Figure 5. The spectrum of ditatpp mirrors that seen for tatpp, obtained as the Zn(II) complex in MeCN, with a large sharp peak in the UV at 350 nm and a structured band in the visible with peaks at 409 nm, 433 nm, and 460 nm. This latter band is assigned as a π - π transition.³⁹ The molar absorptivity of the ditatpp dimer at the highest visible peak (ethanol, λ_{max} 460 nm, $\epsilon = 34,300 \text{ M}^{-1}\text{cm}^{-1}$) is almost twice that of the Zn(II) adduct of tatpp at its highest visible peak (wet MeCN, λ_{max} 445 nm, $\epsilon = 17300 \text{ M}^{-1}\text{cm}^{-1}$).³⁹ The free tatpp ligand is slightly soluble in DMSO and is reported to have two peaks in the visible region at 435 and 460 nm, the latter having a molar extinction coefficient of $10,300 \text{ M}^{-1}\text{cm}^{-1}$ at 460 nm.²⁰ The cause of the discrepancies in peak maxima and molar extinction coefficient could be due to a number of factors including the change in solvent, the presence or absence of the Zn(II) or the difficulty of completely dissolving tatpp, even in DMSO. We postulate that Zn(II) coordination causes a blue shift in the π - π transition due to electron withdrawing effects and it helps to break up any π - π stacking, which can cause hypochromism and is the likely cause of the lower than expected molar extinction coefficient for tatpp in DMSO. It suffices to say that the differences between tatpp and ditatpp are not very large and to a first approximation, the two π systems in ditatpp appear to be electronically uncoupled.

As shown in Figure 5, upon irradiation of degassed ethanol solutions in the presence of TEA (0.2 M), the ditatpp dimer spectrum shows a gradual bleach of the peaks in 405-460 nm region and the appearance of a broad new peak centered at 560 nm, which is assigned to formation of the doubly-reduced, doubly-protonated tatpp unit.^{14,15} While the ethanolic solution does not contain acidic protons, such protons are generated quantitatively via the decomposition of the TEA^{•+} radical cation,⁴⁰ which is generated upon reductive quenching of the photoexcited ditatpp by the TEA. The broad, almost double-

humped peak in the 500-600 region is characteristic of the quadruply reduced and protonated $H_4\text{ditatpp}$, which is shown in the inset in Figure 5. This feature is also seen in the Zn(II) and Ru(II) adducts of tatpp upon double-reduction to the $H_2\text{tatpp}$ complexes.^{20-22,41} The magnitude of the 560 nm peak relative to the bleach at 460 nm is indicative that both tatpp units in ditatpp have undergone double-reduction or a net 4 electron reduction overall to yield $H_4\text{ditatpp}$. The quadruply-reduced product is stable for hours in solution but upon addition of O_2 is rapidly reoxidized to principally to starting material. As seen by the rise in the baseline of the reoxidized species, the reaction is not completely reversible and an estimated 10% of the starting material is lost to side reactions. Notably, during the photoreduction and even after 830 seconds of photolysis, two small but significant peaks are observed in the 800-1000 nm region. Peaks in this region are indicative of the tatpp radical anion in $\text{P}^{3+\bullet}$ (see Figure 1)^{14,16} and are presumably due to the presence of the ditatpp^- or ditatpp^{2-} radical intermediates, which are presumably formed and consumed rapidly as the photolysis proceeds.

The photoreduction product is shown in Figure 6 as the tetrahydro species drawn in the benzoid tautomeric form. It is possible that the complex would prefer the quinoid tautomer, however for spatial reasons only, one tautomer is shown. The reduction is reversible and thus it is possible that ditatpp could be used in a photocatalytic manner. The ditatpp dimer has a number of properties that make it an exciting chromophore for potential light-to-chemical energy conversion schemes. It is freely soluble, contains no expensive or rare metal ions, absorbs in the visible region, and photochemically and reversibly stores up to 4 electrons and protons. These features will be explored in the context of solar energy conversion.

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Figure Captions:

Figure 1. Two electron reduction of the ruthenium-tatpp dimer and the associated nomenclature to indicate the ligand redox and protonation state.

Figure 2. ^1H -NMR of tatpp monomer (top) and ditatpp dimer (bottom). [a] prepared using $\text{d}_3\text{-MeCN}$ and $[\text{Zn}(\text{BF}_4)_2]$ then filtered. [b] prepared using neat $\text{d}_1\text{-CDCl}_3$

Figure 3. Crystal structure of ditatpp at varying angles with solvent removed and axis added for clarity. The crystal has a triclinic unit cell with a $\text{P}\bar{1}$ space group.

Figure 4. ^1H NMR of the tetranuclear complex $[(\text{Ru}(\text{phen})_2)_4(\text{ditatpp})](\text{PF}_6)_8$ in CD_3CN in the aromatic region. (*) indicate the splitting of the larger peaks due to the stereochemical heterogeneity of the complex.

Figure 5. Photolysis of ditatpp (26 μM) at 470 nm in ethanol with 240 mM TEA as a sacrificial donor as a function of time. O_2 added indicates reveals the process is largely reversible. Inset: Chemical reduction 25 μM ditatpp in $\text{H}_2\text{O}:\text{EtOH}$ (1:3) plus 10 mM ascorbic acid to form $\text{H}_4\text{ditatpp}$.

Figure 6. Chemical structure of ditatpp and the quadruply reduced $\text{H}_4\text{ditatpp}$

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6.

Visible light irradiation of the soluble di-tetraazatetrapyridopentacene chromophore in the presence of sacrificial amine donors generates the quadruply reduced compound, storing, in principle, two moles of H₂.