Tuning the reduction of 9,11,20,22-tetraaza-tetrapyridopentacene (TATPP)

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ARTICLE INFO

ABSTRACT

Organic molecules capable of storing and shuttling multiple electrons are desirable for various applications including solar energy conversion, small molecule activation, and water splitting. Here, we demonstrate the ability to photochemically control the reduction of 9,11,20,22-tetraaza-tetrapyridopentacene (TATPP) to form either $TATPPH_2$ or $[TATPPH]^-$, both of which display distinct optical and electrochemical properties, thus providing a rationale for their use in various applications.

Molecular systems capable of storing and shuttling multiple electrons are desirable for various applications including solar energy conversion, small molecule activation, and water splitting.[1–5] While a few notable examples have been reported,[6–10] there continues to be a need to develop systems that can be controlled either by external environmental factors or by solar energy to provide unique tunability and thus reactivity toward specific substrates. Here, we demonstrate that an organic molecule 9,11,20,22-tetraaza-tetrapyridopentacene (TATPP) in solution can be tuned to photochemically store electrons based on the presence of either acid or base. Such molecular systems could yield tunable multi-electron catalysts. MacDonnell and co-workers have demonstrated that the dinuclear ruthenium complexes [(phen)$_2$Ru(TATPP)Ru(phen)$_2$] with TATPP as a coordinating ligand undergoes photodriven two-electron and four-electron reductions in the presence of a sacrificial reductant.[11,12] The processes are completely reversible upon exposure to air and consequently, this complex has the potential to be used catalytically in multi-electron transfer reactions. Surprisingly, not much has been done in terms of understanding the properties of the TATPP ligand alone when exposed to light irradiation. Such information will provide rationale for the design of new systems, while aiding in understanding the use of the ligand in various coordination compounds.

TATPP was synthesized following a modified literature procedure[13] as shown in Scheme 1. Briefly, 1,10-phenanthroline was oxidized to 1,10-phenanthroline-5,6-dione using a sulfuric acid/nitric acid mixture in the presence of potassium bromide. The dione produced in 90% yield was reacted with 1,2,4,5-benzenetetramine tetrahydrochloride in ethanol to produce TATPP in 70% yield. TATPP was characterized by ^1H NMR using a 400 MHz JEOL NMR spectrometer and UV–visible absorbance (Varian Cary 50 spectrometer) spectroscopies. A BAS model CV-50W electrochem-
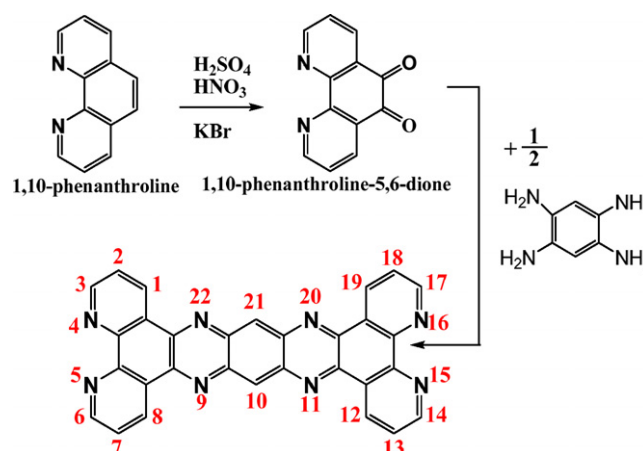

Scheme 1. Synthesis of 9,11,20,22-tetraaza-tetrapyridopentacene (TATPP).

ical workstation in combination with the Varian Cary 50 spectrometer was used for spectroelectrochemical measurements.

Due to the limited solubility of TATPP in most organic solvents, all studies were conducted in dimethyl sulfoxide (DMSO). In general, the irradiation process was carried out in a N$_2$ saturated DMSO solution using a filtered Xe arc lamp (λ >370 nm). Our results showed that TATPP undergoes a photoreduction process, and the resulting products can be tuned based on environmental conditions, in this case, in the presence of either acid or base. Absorption spectra of TATPP in the presence of acid (in this case 1 equiv of HCl) or base (in this case 5 equiv of NaOH) following the irradiation process are shown in Figure 1. The UV–visible absorbance of TATPP alone shows two peaks at 435 nm and 460 nm. The molar absorptivity for TATPP at both 445 nm and 460 nm in DMSO is 10,300 M^{-1} cm^{-1}. Irradiation in the presence of acid resulted in a significant change in the spectrum. Both the 435 nm and the 460 nm peaks disappeared, while a new broad

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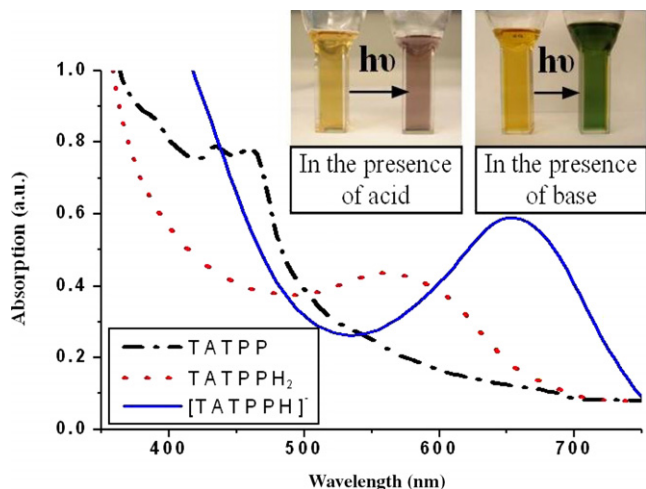
Figure 1. Changes in the electronic absorption of TATPP in DMSO λ_{max} = 435, 460 nm (·–·–); TATPP after irradiation in the presence of acid to form TATPPH$_2$ λ_{max} = 560 nm (····); and TATPP after irradiation in the presence of base to form [TATPPH]$^-$ λ_{max} = 665 nm (—). Spectra were recorded after 30 min of irradiation. The inset shows a photograph of the corresponding color changes that occur after the molecule undergoes photochemical reduction.


Figure 2. Graphical representation of calculation structure of protonation states of TATPP. (The charges on the nitrogens at positions 9 and 11 are drawn for clarity, but were not needed for the calculation.)

band centered at λ = 560 nm, ε_{560} = 6500 M^{-1} cm^{-1} was formed and its intensity increased with increase by irradiation time. An isosbestic point at 490 nm provided evidence for the formation of a new species. The color of the solution following the irradiation process changed from yellow to purple, indicating formation of a reduced TATPP species. The product was stable under a nitrogen atmosphere for days. In the presence of base, the UV–visible absorbance spectrum of TATPP before and after irradiation showed prominent differences. Both the 435 nm and the 460 nm peaks disappeared, and a new peak centered at 665 nm (ε_{665} = 8450 M^{-1} cm^{-1}) emerged. The solution color changed from yellow to green, unlike the observation above, suggesting a different TATPP species being formed in the presence of base. This product was stable under a nitrogen atmosphere for days. The reduction of tetraazapentacene compounds has been investigated by Jenekhe and Dunsch and co-workers.[14,15] They have shown that heterocyclic nitrogen-containing ladder polymers could be protonated either chemically or electrochemically.

To understand the structural changes that occur upon TATPP irradiation, and due to significant limitations in the compound solubility, computational calculations were carried out. All structures were optimized at the B3LYP level of density functional theory. All calculations were done by GAUSSIAN 98 program suite.[16] Initially, the structure was optimized using restricted Hartree–Fock and a small basis set. This structure was then used as the starting point for the density functional calculation. Further optimization was performed using the 6-31G basis set, expanded to include polarization functions (6-31G(d,p)). Frequency calculations at the same level of theory were also performed to confirm that all stationary points were minima (no imaginary frequencies). Application of density functional calculation showed that the HOMO–LUMO band gap of TATPP is 2.80 eV. Computational calculations based on time-dependent density functional theory (TD-DFT) (excluding solvent effects) were applied to provide insights on the reduced TATPP states. Figure 2a shows results of a calculation for a structure in which TATPP was protonated at the nitrogens in positions 9 and 20 or 11 and 22. The calculations predicted that the low energy transitions occur at 561.15 nm, which is within reasonable agreement of the experimental findings. In addition, a comparative structure of TATPP in which two protons were bound to the nitrogens at either positions 9 and 22 or 11 and 20 was calculated. The
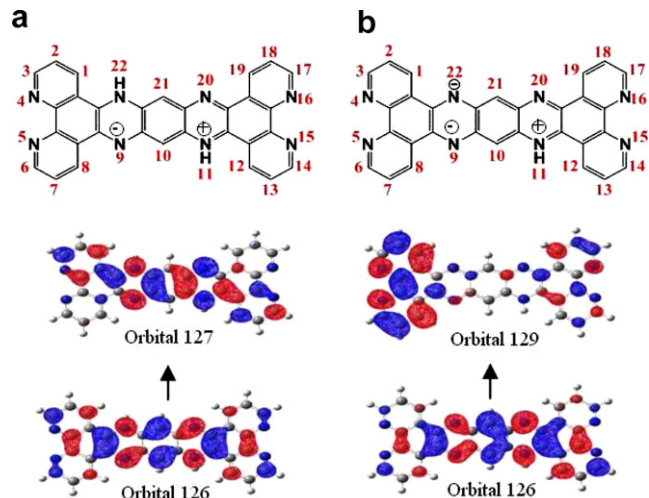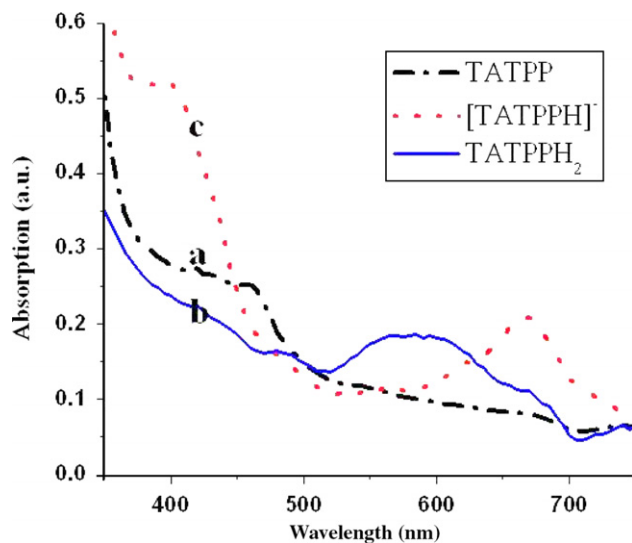
Figure 3. Spectroelectrochemical profile of (a) TATPP in DMSO/0.1 M TBAPF$_6$ with no applied potential (–·–·); (b) upon application of a potential of −0.6 V versus Ag/AgCl to generate TATPPH$_2$ λ_{max} = 560 nm (····), and (c) upon application of a potential of −2.00 V versus Ag/AgCl to generate [TATPPH]$^-$ λ_{max} = 665 nm (—).

data suggested that the latter structure was inconsistent with our results, most likely due to increased polarity that the adjacent protons would induce in the TATPP molecule. In addition, a structure in which TATPP was protonated at all four nitrogens in positions 9, 11, 20, and 22 was calculated.

Such a structure showed an absorbance peak maximum at 740 nm, which is also inconsistent with our experimental data. Thus, the structure shown in Figure 2a is most plausible and further supports the experimental data whereby TATPP irradiated in the presence of acid produces TATPPH$_2$. While phenanthroline protons are known to readily undergo protonation in acidic environments, our results indicate that the corresponding protonated structure would have a much lower energy located in the IR region, and therefore is not consistent with our results. Further computational calculations were performed to determine the energy level of the excited state of a structure in which one proton was bound to one of the pentacene nitrogens and one electron was delocalized in the molecule as shown in Figure 2b. The results predicted that
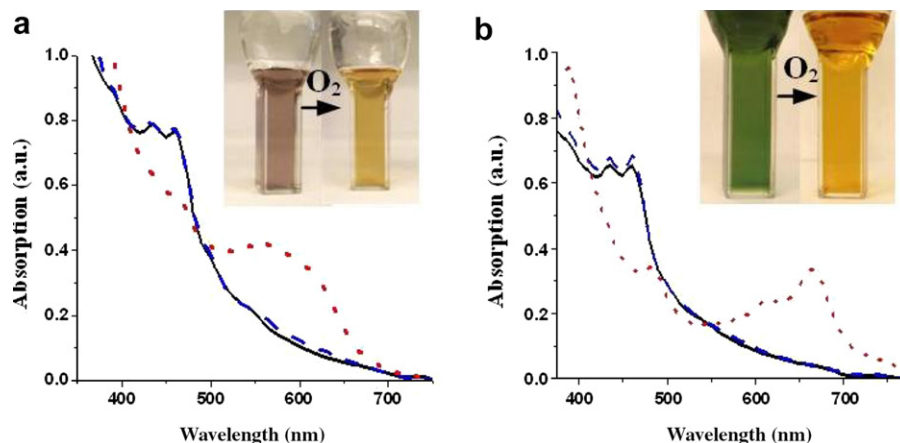
Figure 4. (a) TATPP in DMSO in the presence of acid before irradiation (—); TATPP after irradiation to form TATPPH$_2$ in DMSO solution (⋯⋯), and TATPP generated after exposure to O$_2$ (- - - -). (b) TATPP in DMSO in the presence of base before irradiation (—); TATPP after irradiation to form [TATPPH]$^-$ in DMSO solution (⋯⋯), and TATPP generated after exposure to O$_2$ (- - -). The insets in each figure show a photograph of the corresponding color change of before and after exposure to O$_2$.

the low energy transition occurs at 630.70 nm. Our experimental data showed an absorbance peak at 665 nm. While this value is lower in energy relative to the computational value, we note that the computational calculations, in this case did not account for the solvent effects, but in principle the solvent would further stabilize the structure. Comparative computational calculations in which two electrons were delocalized in the TATPP molecule showed an absorbance maximum at 1325.05 nm, which is inconsistent with our experimental data. Both the computational results and the experimental results suggest that the structure generated when TATPP is irradiated in the presence of base is [TATPPH]$^-$. Furthermore, calculations in which the phenanthroline nitrogens were protonated were conducted, but the results were inconsistent with our experimental data.

$$TATPP \xrightarrow{H^+, h\nu} TATPPH_2 \underset{H^+}{\overset{OH^-, h\nu}{\rightleftharpoons}} [TATPPH]^- \qquad (1)$$
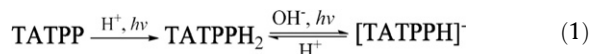
The experimental data show that the formation of either of the two photo-generated products can be controlled by environmental conditions, that is, TATPPH$_2$ generated in the presence of acid can be easily converted to [TATPPH]$^-$ by simply adding excess base followed by irradiation, while [TATPPH]$^-$ can be converted to the protonated product TATPPH$_2$ by simply adding acid as shown in Eq. 1.

In an effort to determine the redox and protonation behavior of TATPP system, spectroelectrochemical analysis of TATPP was further investigated. Spectroelectrochemistry confirmed the findings of reduction states of TATPP. There are two specific reduction potentials observed. When a potential of -0.60 V versus Ag/AgCl was applied to a solution of TATPP in DMSO/TBAPF$_6$, and equilibrium was attained, the solution color changed from yellow to purple, and the spectrum shown in Figure 3 (solid line) was generated. Application of a more negative potential of -2.00 V versus Ag/AgCl to TATPP in DMSO/TBAPF$_6$ and allowing the solution to acquire equilibrium resulted in a color change from yellow to green and the spectrum shown in Figure 3 (dotted line) was obtained. Both these spectra are consistent with reduced TATPP products as shown by UV–vis data acquired following irradiation in either acid or base (Fig. 1).

The ability to store electrons in a molecule and dissipate the electrons as needed has several significant implications including small molecule activation, solar energy conversion, and in electronic devices. To investigate whether the electrons stored in either TATPPH$_2$ or [TATPPH]$^-$ could be transferred to a substrate, each solution was exposed to dioxygen.[17] In each case, the solutions changed color. In the case of TATPPH$_2$ the solution color

changed from purple to yellow, while in the case of [TATPPH]$^-$ the solution color changed from green to yellow as shown in the insets of Figure 4a and b, respectively. The UV–visible absorbance profiles in both cases showed that the species had been oxidized back to TATPP (Fig. 4a and b). These data are similar to earlier work by McGovern et al. who investigated the photoreduction of DPPZ and its re-oxidation using dioxygen.[18] The oxidized TATPP molecule could be irradiated again and subsequently oxidized by dioxygen and the process could be repeated up to ten times with no observed degradation of the TATPP molecule.

In summary, we have demonstrated that TATPP can be selectively reduced in the presence of either acid or base to generate TATPPH$_2$ or [TATPPH]$^-$, respectively. The spectroelectrochemical data suggest that [TATPPH]$^-$ is a stronger reducing agent relative to TATPPH$_2$. The ability to control the structure of reduced TATPP photochemically provides a means to rationally use the molecule either alone or in coordination complexes to design various systems for advanced applications.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.142.

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