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Biocatalytic Synthesis of the Conjugated Bridging Ligand Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tpphz) and a Dinuclear Ruthenium Complex

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We have synthesized a fully conjugated aromatic bridging ligand, tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tpphz), and a dinuclear ruthenium complex using Hematin as a biocatalyst.

There has been tremendous interest in multinuclear complexes synthesized using conjugated bridging ligands for applications in photoinduced energy transfer and sensitization processes.[1] These systems have been extensively studied for their long distance electron transfer due to their photostability. In particular, Ru(II) complexes with polypyridine ligands are well studied for their efficient photophysical and photoelectrochemical properties for their potential applications in electronic and photomolecular devices.[2] Toward preparation of multinuclear systems with extended conjugation, a variety of bridging ligands were used.[3] Among them, the recently developed tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tpphz) is a very interesting bridging ligand due to its favorable structural features.[4]

There have been a few reports on using tpphz for preparing ruthenium and osmium homometallic and heterometallic multinuclear complexes for study as molecular switches for DNA,[5] for stereospecific synthesis of oligonuclear Ru(II) complexes,[6] and for the synthesis of soluble, well-defined ruthenium coordination polymers.[7] Ru complexes with tpphz have been proven to bind DNA very strongly due to the intercalation of the tpphz ligand between adjacent base pairs of the duplex. Recently Chiorboli et al.[8] reported ultrafast processes in bimetallic dyads with tpphz as the brdging ligand. This work demonstrated the importance of using tpphz ligand for intramolecular photoinduced energy or electron-transfer studies.

Akkara et al.[9] showed that hematin (hydroxyl ferriprotoporphyrin), the catalytic center in certain enzymes, can undergo redox changes similarly to horseradish peroxidase (HRP) in the presence of H_2O_2 in organic solvents such as DMF. Since then, hematin and modified hematin have been used as catalysts for the synthesis of several conducting and photonic polymers.[10] In our recent study, we used hematin as a biocatalyst for the synthesis of a ruthenium polypyridyl complex based macrodye for photovoltaics applications.[11] However, to date hematin has not been used for the synthesis of small molecular systems. Thus we considered this facile and biocatalytic approach for the synthesis of these promising photoactive materials.

In this Communication, we report for the first time hematin-catalyzed synthesis of the small molecular system and the conjugated bridging ligand, tpphz and a dinuclear ruthenium complex. The ruthenium dinuclear complex was

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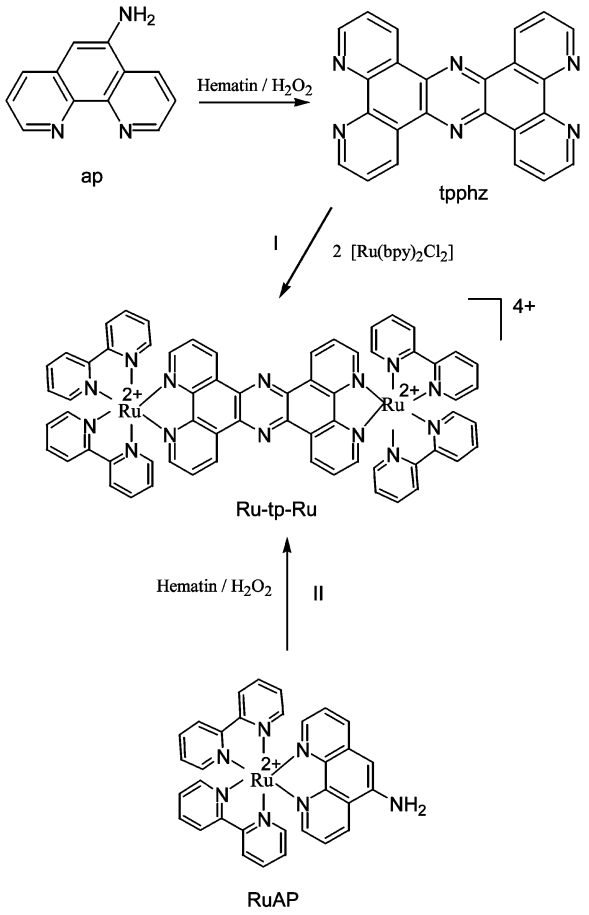
Scheme 1. Synthesis of tpphz and Ru-tp-Ru



also synthesized using the known traditional chemical complexation of tpphz for comparison.

The synthesis of tpphz is carried out as follows (Scheme 1). 5-Amino-1,10-phenanthroline (ap) (Polysciences) (0.2 g) and 3 mg of hematin (Sigma) were dissolved in 5 mL of *N*,*N*′-dimethylformamide (DMF) at room temperature, and 0.1 mL of 30% H_2O_2 was added dropwise to initiate the reaction. The reaction was monitored by UV−vis absorption spectroscopy. After stirring for 24 h, the pale yellow precipitate formed was filtered and washed with methanol and diethyl ether and purified by recrystallization from chloroform. Yield = 0.1 g (25%). ^{1}H NMR (250 MHz, $CDCl_3$): 9.67 (dd, 4H), 9.39 (dd, 4H), 7.90 (dd, 4H). EI-MS (*m*/*z*): 384 (100).

The dinuclear complex $[(bpy)_2Ru^{II}(tpphz)Ru^{II}(bpy)_2](PF_6)_4$ (Ru-tp-Ru) was also biocatalytically synthesized as described for tpphz, using the monoruthenium complex $[Ru^{II}(bpy)_2(ap)](PF_6)_2$ (RuAP, Scheme 1), which was prepared following the reported procedure[11] (where bpy = bipyridyl). The reaction proceeds similarly to tpphz in methanol, and product precipitates as a red powder. Ru-tp-Ru was also prepared using tpphz and $[Ru^{II}(bpy)_2Cl_2]$ (Aldrich) following the reported procedure[4b] for comparison.

The UV−vis absorption spectra of the starting compounds, ap and tpphz, measured in DMF solution, are shown in Figure 1. The sharp peaks observed at 388, 378, and 368 nm are due to n−π* transitions, and a peak at 308 nm is

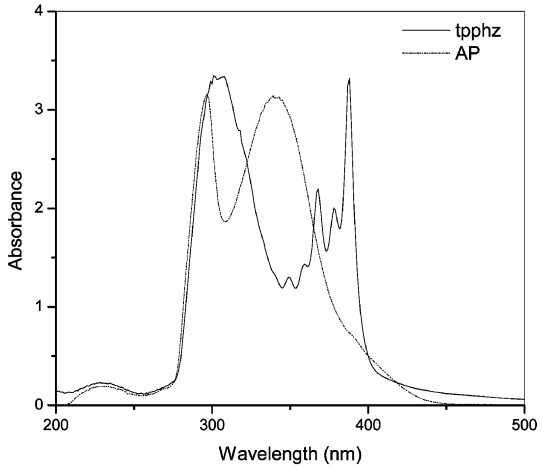


Figure 1. UV−vis absorption spectra of AP and tpphz.

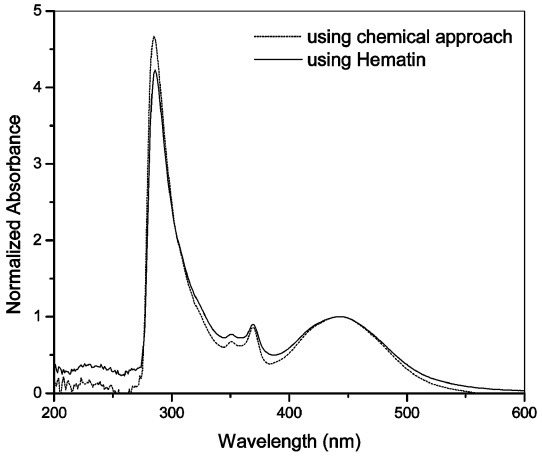


Figure 2. UV−vis absorption spetra of Ru-tp-Ru.

attributed the $\pi-\pi^*$ transitions. These spectra are consistent with earlier reports on tpphz.[4b] The characterization of the dinuclear complex prepared from both routes was found to be quite similar.[4b,12]

The UV−vis absorption spectra of the dinuclear complex prepared from different methods are shown in Figure 2. The spectra are identical, and the MLCT absorption and emission maxima measured in acetonitrile solution are 445 and 670 nm (excited at 445 nm), respectively, and are also consistent with the previous reports.[4b]

The earlier chemical methods to prepare tpphz used either high reaction temperature (180 °C) or multistep synthesis.[4b] One of the most attractive features of our biocatalytic method is the extremely simple synthetic protocol involved. The reaction is a single step and can be carried out under extremely mild and environmentally friendly conditions at room temperature. The advantage of this synthesis is that there were no other side products observed in the precipitate that was formed from the reaction solvent. Though the reaction yields (calculated on the basis of the precipitate

(12) ^{1}H NMR spectra of Ru-tp-Ru from both methods were identical (250 MHz, CD_3CN): 10.01 (dd, 4H), 8.62 (d, 4H), 8.33 (dd, 4H), 8.20 (dd, 4H), 8.17 (td, 4H), 8.0 (d, 4H), 7.91 (d, 4H), 7.78 (d, 4H), 7.55 (ddd, 4H), 7.32 (ddd, 4H). Anal. Calcd for the complex from route II, $C_{64}H_{44}F_{24}N_{14}P_4Ru_2 \cdot 2H_2O$: C, 42.07; H, 2.65; N, 10.73. Found: C, 42.33; H, 2.55; N, 9.65.

collected) are currently low, there is a high possibility to improve the yields upon modification in the workup procedure. The synthesis of dinuclear complex Ru-tp-Ru using this biocatalytic method is novel and can be explored further.

Spin density calculations which were performed using AM1, a semiempirical computational method,[13] on ap to investigate the reaction sites strongly support our observation. The amino nitrogen and the adjacent carbon radicals have high spin density values (C, 0.53; N, 0.80) as shown by yellow color spheres on these atoms in Figure 3. This indicates that the reactivity of these two atoms is high for the formation of the dimer, tpphz. There could be an intermediate state where another hydrogen on the amino group is removed in the biocatalytic reaction to facilitate the formation of a stable aromatic system, tpphz.

These results open new possibilities toward an alternative, low-cost and efficient biocatalytic route to synthesize conjugated aromatic bridging ligands and multinuclear systems for various applications. We are currently exploring the possibilities of synthesizing other interesting conjugated bridging ligands and ruthenium multinuclear systems for dye-sensitized photovoltaic applications.

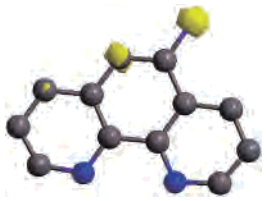


Figure 3. Calculated spin density (yellow spheres) on ap molecular radical.

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(13) Austin Model 1 in MOPAC, Fujitsu Inc.