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**Synthesis and Metallation of TPP**



**Experimental:**

*Week #1:* To a 250ml round bottom flask was added 135ml of propionic acid, 0.036mol (2.5ml) of pyrrole, 0.0356mol (3.63ml) of benzaldehyde, and a boiling stone. A condenser was attached to the round bottom flask, and the round bottom flask was placed in a round bottom flask heater. The heater was turned on and the mixture was heated under reflux for 30min. While the mixture refluxed, the magnetic susceptibility of an iron sample was taken. After 30min, the mixture was allowed to cool for 40min to room temperature, then cooled in an ice bath for 10min, until crystallization occurred. The product was filtered over a Buchner funnel and washed with methanol and hot deionized water. The dry product was placed into a vial and allowed to dry for an additional week. Collected was 0.125g of product. Percent yield was 2.26%.

*Week #2:* The product from the previous week was weighed before obtaining a 100ml round bottom flask. The round bottom flask was placed into a round bottom flask heater sitting on a stir plate. To the round bottom flask was added a stir bar, 0.813mmol (0.5g) of TPPH2 product, and 50ml of DMF. Another groups TPPH2­ product was used, because our group was unable to synthesize enough. A UV light was obtained and used to illuminate the mixture, which had a slight red glow under the UV light. To the mixture was added 0.214g of unknown A. A condenser was added to the flask and the mixture was heated to reflux for 30min. The mixture was shown under UV light again, and still had a slight red glow. While the mixture refluxed the magnetic susceptibility of the product from the previous week was taken. The mass susceptibility was -3.94x10-7 cm3/g, and the molar susceptibility was -2.42x10-4 cm3/mol. After 30min of reflux, the round bottom flask was placed into an ice bath and 50ml of DI water was added. It was allowed to cool for 15min. Once cool, the mixture was filtered over a Buchner funnel and washed with DI water. The product was put into a vial and allowed to dry for a week, before being weighed. Collected was 0.524g of product. Percent yield was 95%.

*Week 3:* The product from the previous week was analyzed with IR spectroscopy, UV-Vis spectroscopy, NMR, and GCMS. Magnetic susceptibility was recorded to be Xg = .

**Spectra:**

*MTPP:*

1H NMR (CDCl3; 300MHz) ? 8.97 (s, 8H); 8.25 (d, *J*=7.6Hz, 8H); 7.79 (s, 8H); 7.77 (s, 4H).

UV-Vis (EtOH): λmax = 550nm, ε = 14,240 M-1 cm-1

GC-MS: (m/z): 676 (65%, M+), 675 (21%, M+-H)

*H2TPP:*

1H NMR (CDCl3); 300MHz) ? 8.90 (s, 5H), 8.27 (d, *J*=7.7Hz, 5H), 7.80 (s, 5H), 7.78 (s, 3H), -2.69 (s, 1H)

UV-Vis (EtOH): λmax = 516nm, ε = 16,010 M-1 cm-1

IR (HATR) *v* (cm-1): 3314 (w, N-H str)

**Discussion:** In the first week we were able to make only 0.125g of product, which is a 2.26% yield. The poor yield is most likely because our mixture took a while to cool, and it might not have had enough time in the ice bath. The product was confirmed to be H2TPP through IR, NMR, and UV-Vis. In the second week we received 0.524g of product, a 95% yield. The product was confirmed to be Zn-TPP by GC-MS, IR, NMR, and UV-Vis.

The NMR data for the H2TPP showed peaks at 8.9, 8.27, 7.8, 7.78, and -2.96. According to an article by Falvo and Mink, H2TPP should have peaks at 8.85, 8.28, 7.75, 7.77, and an N-H peak at -2.79 (Falvo; Mink, 238). All of these peaks match up well with the ones in our NMR. The NMR for our M-TPP should, according to another article, by Marsh and Mink, should look very similar to the H2TPP NMR, except without the N-H peak at -2.79, and with a slightly more up field or down field peak for the H on pyrrole, depending on the metal. Our M-TPP had peaks at 8.97, 8.25, 7.79, and 7.77. This both confirms that the reaction worked, because of the lack of an N-H peak, and that the metal might be Zinc, because the H-pyrrole peak was slightly ore down field than on H2TPP, as shown in the literature (Saucedo; Mink).

The IR spectroscopy for H2TPP showed that there was a peak at around 3300 for the N-H bond. This peak was absent in the M-TPP IR spectrum, confirming that the reaction was successful and the product was M-TPP.

The UV-Vis spectrum showed that H2TPP absorbed light at wavelengths of 648nm, 590nm, 550nm, and 516nm. According to an article by Marsh and Mink, H2TPP should have intense absorption between 500nm and 550nm, while it should have less absorption between 590nm and 650nm. The data that was collected matches up with these number very well. For the M-TPP, there were absorption peaks at 550nm and 594nm. According to the same article as above, Zn-TPP should have peaks between 550nm and 600nm, while Ni-TP should have a peak around 525nm. The collected data matches up better with the Zn-TPP data, helping confirm that Zn-TPP was the product that was recovered. This article also says that Zn-TPP will glow under UV light, which the product that we received did (Marsh; Mink, 1189).

Our product was also confirmed to be Zn-TPP by the magnetic susceptibility, which was

**Questions:**

1. H2TPP and M-TPP do not belong to the same point group, because the H2TPP has two hydrogens across from each other, making the C4 rotation of the M-TPP not possible.
2. Instead of using normal benzaldehyde, you would use a benzaldehyde with an OMe group para to the aldehyde.
3. .
4. Fluorescence is when UV radiation is absorbed by electron, raising them to an excited state. The electrons then drop from this excited state, and in doing so release light. Phosphorescence is when electrons are raised in energy level, but cannot immediately drop back down, because the electrons spin is flipped. In order for the electrons to release their energy, they need to reverse their spin again. This takes time so the energy is released slowly, meaning that the molecule emits light even after the UV light has gone. Both the H2TPP and Zn-TPP were fluorescent.