Supramolecular Electronics Derived from Porphyrin-like Pigments

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The field of organic based electronics has become a blossoming area of intensive study during the past decade. The promise of a cheaper and easier-to-process alternative to inorganic based semiconductor materials makes these materials highly desirable.[1] Additionally, organic based electronics can be made into flexible structures, allowing for the fabrication of visual displays that can be folded or rolled-up. The two most widely investigated classes of organic materials have been small-molecule and polymer based. While small molecule based materials are easily purified and form single crystalline materials with high mobilities, they are energy intensive and difficult to process.[2] Conversely, polymeric materials are easily processed and synthesized, yet their heterogenous composition of molecular weights can affect carrier mobility through low crystalline ordering.[2] The burgeoning area of interest involved with supramolecular chemistry may help to alleviate the setbacks of molecular and polymeric organic electronics. Supramolecular based electronics involve non-covalent ordering of building blocks that can create diverse, responsive, and ordered structures.[3] The most well-studied interactions include hydrogen bonding, host-guest chemistry, and π-π interactions.[4] These self-assembled structures hold promise as complex, organized, one or two dimensional structures can be formed from single molecules over relatively long distances.[5] The precise ordering of structures makes them desirable for directional exciton or charge transport which is fundamental to many organic electronic devices such as photovoltaics, organic light emitting diodes (OLEDs), and organic field-effect transistors (OFETs).[6]
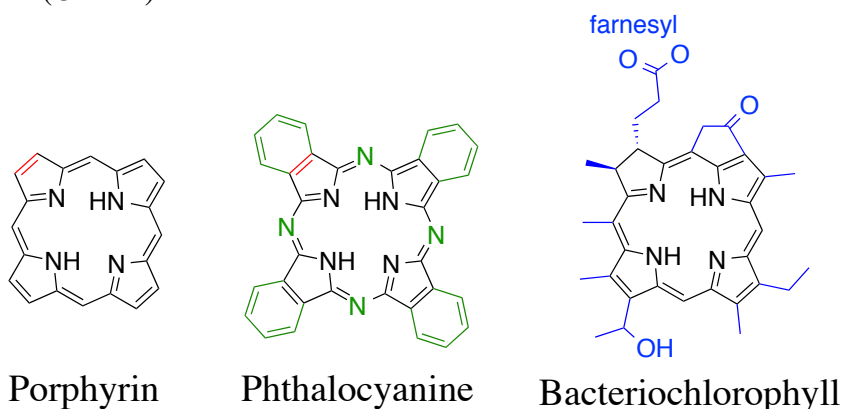

Figure 1. Structures of various porphyrin derived pigments.

Supramolecular structures used in electronic devices are almost invariably derived from highly planar, π-conjugated molecules. Some of the most promising systems are comprised of molecules such as perylenes,[7] hexabenzocoronenes,[8] and oligothiophenes.[9] The utility of these materials is often measured by comparing carrier mobilities through various methods such as time of flight (TOF), or more recently, through pulse radiolysis time resolved microwave conductivity (PR-TRMC) and flash photolysis TRMC (FP-TRMC). The latter two techniques involve the formation of free charge carriers through either a high energy electron or light pulse. This pulse creates charge carriers within a very small domain of the material, whose decay can be monitored using microwave irradiation. This provides an optimal technique for probing the carrier mobilities for highly ordered structures on the molecular scale without external electrodes.

Besides the typical systems mentioned previously, there is a growing interest in porphyrin and related molecules. Porphyrins are naturally derived macrocyclic, planar, π-conjugated molecules, the most notable example being heme, which contains the Fe^{2+} ion and is responsible for the red pigmentation of blood. Biologically, porphyrins and related molecules are known for their redox activity and high absorption coefficients. Specialized derivatives such as chlorophyll and bacteriochlorophyll are found in naturally occurring light harvesting systems in plants and bacteria. These properties make porphyrin-like molecules exciting new avenues for designing optoelectronic materials.

Naturally derived porphyrin based molecules, such as chlorophyll, lend further utility towards the design of optoelectronic devices as they possess high stability towards various conditions such as pH temperature and under facile modification.[10] Recently, the use of a porphyrin based supramolecular system in combination with a hydrophilic wedge and fullerene have shown potential for use in such devices.[11] This amphiphilic porphyrin-fullerene dyad contains one chiral center which, interestingly, dictates the supramolecular structure formed. As a racemate, only nanometer sized (300 nm) spherical assemblies are formed. The electron transport properties of these supramolecular spheres is extremely low, showing low mobilities. In contrast to the racemate, self-assembly of the pure enantiomer forms long nanofibers up to 10 μm in length. These show excellent electron and hole mobilities, measured by TOF, of 0.14 and 0.10 cm^2 V^{-1} s^{-1}, respectively. Modification of the structure through the chelation of Zn^{2+} ions, and changes in linker structure further tailor the system. Two new zinc based porphyrin dyads containing either an ester or alkyne linkage showed vastly different self-assemblies.[12] X-ray diffraction (XRD) and transmission electron microscopy (TEM) support the formation of nanotubes; however, the structure of the nanotubes differ significantly between the two molecules. The packing in the ester-based linker gives large bilayer nanotubes, while the alkyne-based linker shows smaller nanotubes with monolayer packing. FP-TRMC was used to determine the charge carrier mobilities of each assembly, both of which showed relatively high conductivities of 1.02×10^{-3} cm^2 V^{-1} s^{-1} and 0.16×10^{-3} cm^2 V^{-1} s^{-1}. These values do not take into account the quantum efficiencies of the photoexcitation and comparison on equal terms to the chiral based system mentioned previously (1.2×10^{-4} cm^2 V^{-1} s^{-1}) shows that the former assemblies are superior in terms of charge transport.

One of the recently discovered and exciting systems for supramolecular electronic applications are those based off of bacteriochlorophyll. Bacteriochlorophyll is a porphyrin analog with several unique features, such as several chiral centers, a ketone functionality, and one hydrogenated pyrrole ring. In bacteria these are assembled without the assistance of a protein scaffold, and are thought to form tubular rods which then assemble into stacks, according to the current model.[13] A synthetic zinc based bacteriochlorophyll mimic to the naturally occurring molecule was synthesized in which a hydrophobic dendron wedge was attached to the bacteriochlorin ring. Concentration and temperature dependent UV spectra indicated the formation of supramolecular J-aggregates, which are excitonically coupled aggregates.[14] Key features of these types of aggregates include a bathochromic shift in UV absorption with a sharp peak.[15] This indicates that the bacteriochlorin compounds form a close-packed supramolecular structure. AFM images confirmed the formation of supramolecular rod-like structures. The PR-TRMC measurements showed that this material was an excellent charge carrier, with carrier mobilities of 0.07 cm^2 V^{-1} s^{-1}.[16]

Supramolecular systems such as these have also been extensively useful to study structure-function relationships. One key advantage of supramolecular systems is that one can tune the system by making small changes to monomer structures. Deriving relationships between small chemical modifications and subsequent structure are key, as they ultimately affect the

function of the material. In the previously mentioned bacteriochlorin system, the modification of the hydroxyl functionality, which plays a key role in self-assembly, to a non-hydrogen bonding methoxy group shifts the structure to a two-dimensional sheet-like structure.[17] Surprisingly the mobilities of these structures were four times greater, reported to be 0.28 cm^2 V^{-1} s^{-1}.[16] The rationale for such observations is still an intensive area of research. Furthermore, the replacement of the hydrophobic wedge from bacteriochlorin assemblies can create stable, water-soluble, supramolecular structures. TEM micrographs clearly show a tube-like morphology. The UV-Vis absorption spectrum also shows the formation of a J-type absorption band. The charge carrier mobility of this structure was also measured by PR-TRMC to be 0.03 cm^2 V^{-1} s^{-1}.[13] Further demonstration of the conductivity of the nanotubes was performed using conductive AFM (c-AFM).[13] Briefly, the nanotube is positioned such that part of it resides on a non-conductive surface, and the other part on a conductive surface. The tip of the AFM probe is then made to contact the nanotube and the current can then be analyzed on the surface. c-AFM measurements show that upon placing the tip on the nanotube, the conductive surface of the substrate shows a current signal.

Further development of these supramolecular electronic systems will be an active area of research over the coming decade, as fabrication of inorganic electronic devices continues to become more expensive. The advantages of organic based electronic devices, such as physical flexibility and low cost, make these materials highly desirable. Supramolecular devices hold greater promise yet in addressing the synthesis of ordered structures that may increase carrier mobilities through simple self-assembly.

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