Towards artificial photosynthesis : resolving supramolecular packing of artificial antennae chromophores through a hybrid approach

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Chapter 5

Conclusions and outlook

5.1 Discussion

The primary source of energy in the universe is the sun and to harvest it for the production of clean fuel requires artificial antenna complexes. Structural analyses of chromophores that are compatible for light harvesting were performed. At a later stage, such chromophores could be integrated into to the artificial light harvesting antenna modules of a solar fuel cell device. For the three different supramolecular self-assemblies, building blocks in each packing are derived from one of the most frequently occuring space groups in the 230 crystal classes. For moderately sized organic molecules the packing generally involves screw axes and glide planes that have a translational component to accommodate the steric hindrance of functional motifs to achieve low energy and high density. Here however glide planes account for the steric hindrance in DATZnS(3′-NMe) and DATZnS(4H) using $P2/c$ space group and an inverse symmetry that results in the centerosymmetric dimers with P-1 space group for D1A2. Knowledge about the packing is essential for the design of solar fuel cells since it plays a crucial role in bridging a photo electrode comprising artificial light harvesters to a catalyst motif. In this thesis, a methodology is developed involving the integration of electron microscopy and solid state NMR spectroscopy, in addition to molecular modelling with force fields to converge on reasonable packing. This methodology is used to understand the packing in self-assembled supramolecular light harvesters DATZnS(3'-NMe) - chapter 2, D1A2 - chapter 3 and DATZnS(4H) - chapter 4.

Symmetry constraints obtained from CP/MAS NMR, systematic absences obtained from the Fourier transformation of the diffraction patterns and density of the sample helps to converge on the $P2/c$ space group for describing the packing of DATZnS(3′-NMe).[1] The supramolecular scaffold is stabilized by sheets of dipoles running in mutually opposite directions. Parallel stacking of NDI and the alignment of electric dipole moments perpendicular to each other in layers of DATZnS(3'-NMe) forms a grid, which may have future application in the design of a solar fuel cell device (Figure 2.5 and 5.1). Packing of DATZnS(3′-NMe) in parallel molecular

stacks in an antiparallel lamellar framework is validated, by comparing the strength of the heteronuclear dipolar coupling from an LGCP build up curve experiment and simulation, for selected ^{1}H-^{13}C pairs. Simulation of a DATZnS(3′-NMe) diffraction pattern using CrystalMaker generates the same systematic absence as observed in the Fourier transformation of the TEM image, which validated the proposed packing (Figure 2.4). Moreover, simulation with CrystalMaker is successfully used to generate the preferred orientation of the material on the surface, though there is a possibility to have the existence of polymorph forms. Recognition motif formed between the salphen and NDI is the driving force for the aggregation along the principal axis of the molecule. Intermolecular correlation peaks from ^{1}H-^{13}C HETCOR at the higher mixing time of 4 ms confirms the recoginition motif and the folding of tails in between the stacks along the phenazine moiety. This supramolecular recognition motif is a characteristic of the packing of DATZnS(3′-NMe). The Lewis acid character of the Zn^{2+} can be used to attach a catalyst to this scaffold.

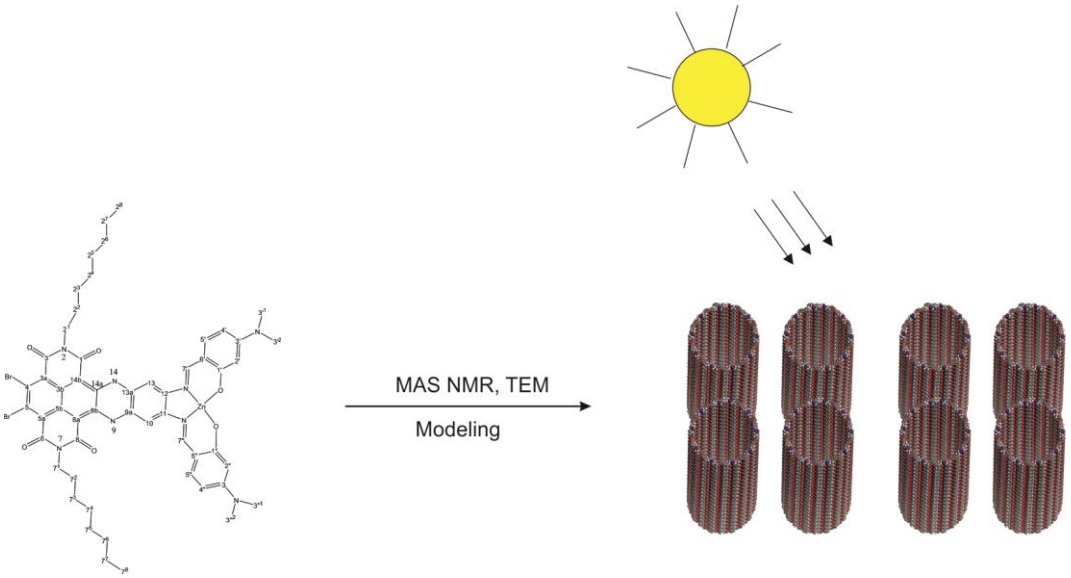

Figure 5.1 Schematic representation of how CP/MAS NMR in conjunction with TEM and molecular modelling allows to converge on a *P*2/*c* space group which could be modified into nanorods for attaching to a photo electrode surface. Dipole moments are aligned along the surface of the rods.

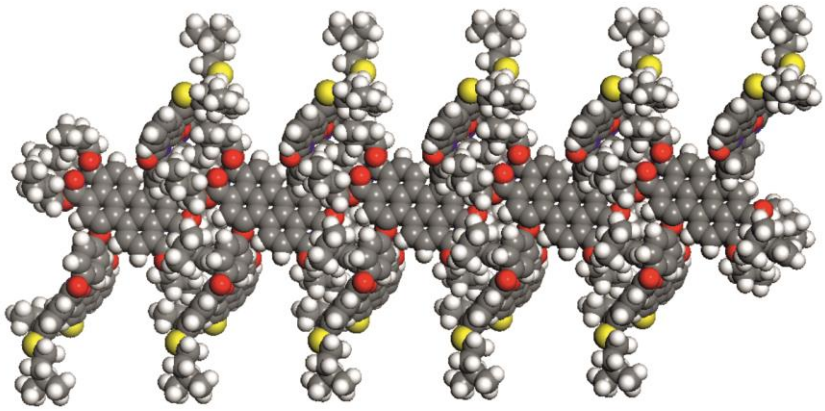

Figure 5.2 The stacking of D1A2 in one dimension showing the formation of rod type packing for perylene core and naphthalene monoimides projecting outwards.

In the case of D1A2 specific heteronuclear correlations point to centrosymmetric dimer formation, from P and M enantiomers. Computational integration of ENC and MAS NMR with a biased molecular replacement approach is performed to determine the packing of D1A2. Unit cell parameters obtained from ENC with density and HETCOR analysis converges up on *P*-1 packing with antiparallel stacking. The rod type structure of D1A2 in the solid state leads to the formation of rows of dimers, with naphthalene monoimide antennas projecting out (Figure 5.2). This will serve as an antenna system in which light energy is harvested by naphthalene monoimide and fed into the system with nano rods of perylene through FRET. D1A2 molecules exhibit good overlap between the donor's emission and the acceptor's absorption, which is a prerequisite for an efficient excited energy transfer (EET) by the Forster mechanism.[2,3]

A homology approach is proposed in chapter 4 for the DATZnS(4H) molecule based on the DATZnS(3′-NMe) parent compound in chapter 2. Distance constraints obtained from CP/MAS NMR data with limited data from TEM are used to put forth packing in the same *P*2/*c* space group but with a different positioning of the molecules in the unit cell where the axes were changed accordingly. Since the structure of DATZnS(4H) is a homologue of the DATZnS(3′-NMe), this implies that the NCH_3 functional group can be used to steer the packing from a parallel sheet in DATZnS(3′-NMe) to an antiparallel sheet in DATZnS(4H). Thus, chemical

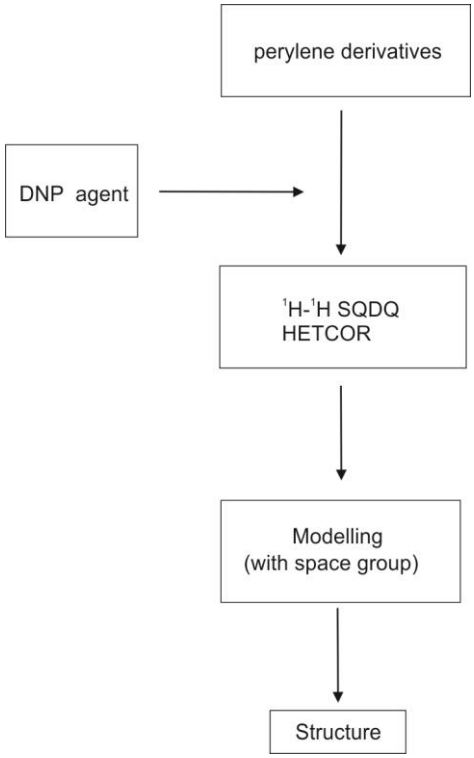

Figure 5.3 Schematic representation of DNP enhanced structure determination. It involves incorporating DNP agents into perylene derivatives by wet impregnation or glassy formation. Once it is successfully fused with the sample, a ^{1}H-^{1}H SQDQ could be employed, which helps to get highly resolved intermolecular correlation peaks. DNP could enhance the signal intensity up to 100 times.

substituents can be utilized to steer the alignment of the dipole between parallel and antiparallel in a sheet. We anticipate that this understanding is key to the chemical design of supramolecular scaffolds as an artificial antenna complex for the organic solar fuel cell device concepts.[4-7]

5.2 Future experiments

5.2.1. DNP enhancement

MAS NMR spectroscopy with Dynamic nuclear polarization (DNP) has the potential to enhance NMR signals by several orders of magnitude. High speed spinning Single Quantum Double Quantum (SQDQ) ^{1}H-^{1}H spectroscopy with DNP will help to get highly resolved intermolecular correlations.[8-11] DNP as explained by Overhauser in 1953 and demonstrated by Carver and Slichter involves the transfer of electron polarisation from a radical to neighbouring nuclei of interest resulting in enhancement of intensity.[12,13] DNP is usually achieved by a suitable polarising agent, which is excited by the irradiation of a sample with microwaves from a

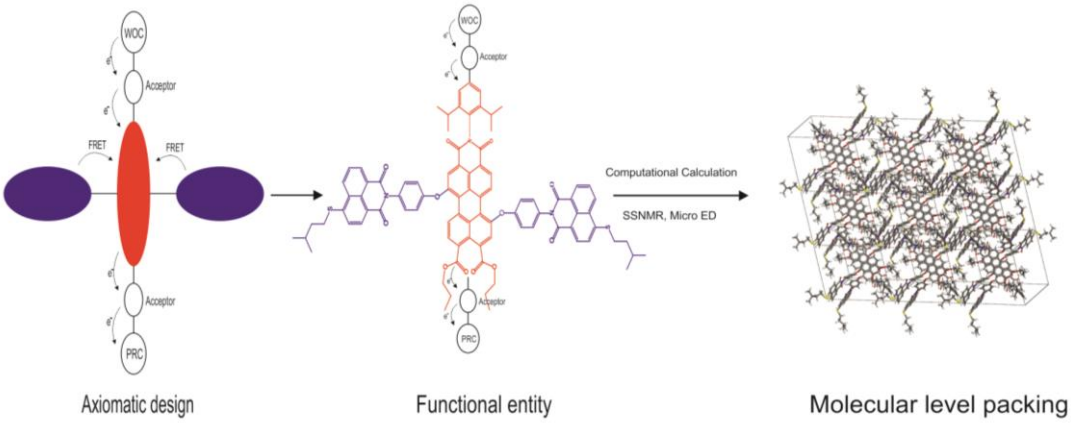

Figure 5.4 Axiomatic design of a solar fuel cell device using the D1A2 molecule. Packing studies give an insight in to the molecular level arrangement of the perylene derivative and its associated naphthalene monoimide functional motifs. This insight can be used in the design of modular photo electro chemical device concepts.

gyrotron source followed by the acquisition of the spectra. A combination of radical, polarising agent 4-hydroxy-TEMPO (TEMPOL) and ortho-Terphenyl (OTP) could be the best DNP agent as described in the work of Ong *et al*.[8] Researchers tried to incorporate DNP on the surface studies and structural analysis of proteins.[14] For unlabelled materials, DNP enhancement is so strong that you can incorporate DNP agents to SQDQ experiments, which lead to a much better resolution. This kind of methodology development will help to increase the accuracy and to resolve the packing of heterogeneous structures, which are inaccessible with the current state of the art. Since although these experiments are emerging, I foresee that they will be more powerful when combined with diffraction methods that discussed in this thesis (Figure 5.3). At a later stage, this could be extended to understand the mechanism on the electrode surfaces.

5.2.2 Design of a solar fuel cell device

Axiomatic design is a well-known concept in engineering, which is able to produce highly complex devices. I foresee the development of structure based strategies, involving bioinspired design concepts for crystal engineering to guide the fabrication of chromophores with structure determination facilitating the

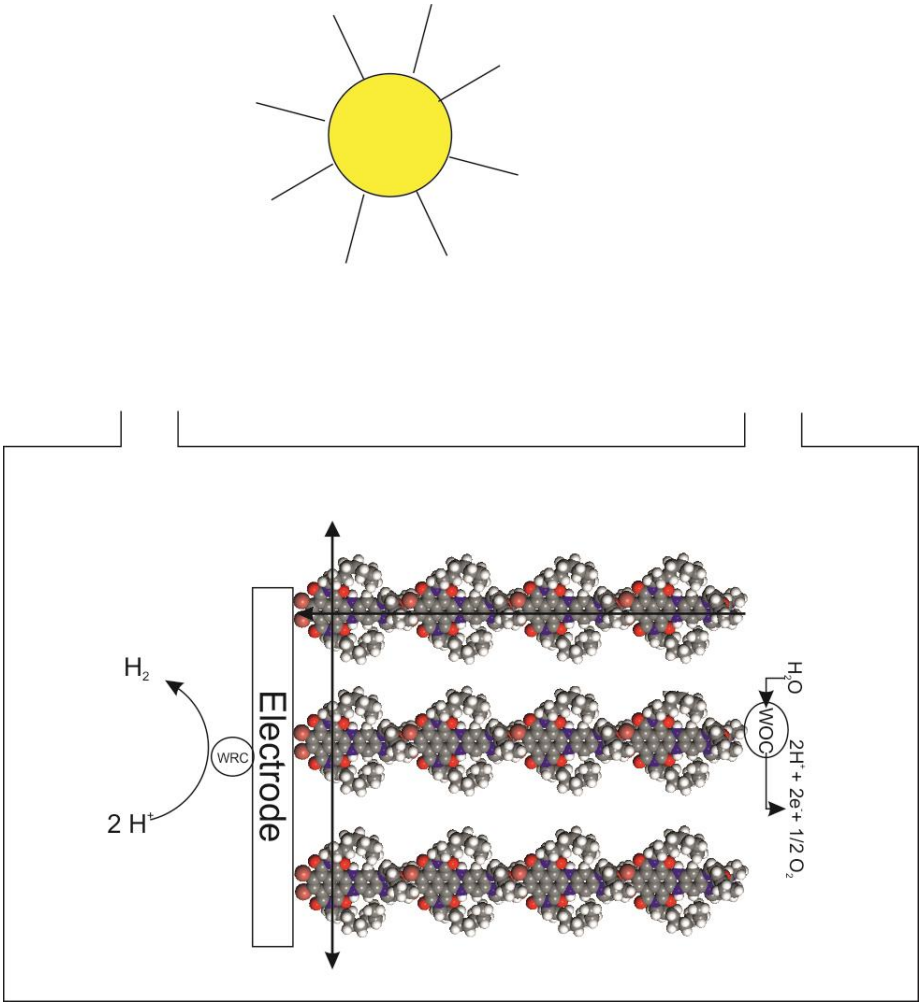

Figure 5.5 Schematic design of a solar fuel cell device. The fused DATZnS chromophore derivatives could be modified to attach to the electrode surface. A water oxidation catalyst could be grafted to the antenna complex by using the Lewis acid property of salphen.

fabrication of chromophores that can be synthetically modified for coherent transfer of electrons. It is important that D1A2 dimer operates in synergy for transfer of energy and can be optimized further. In the design matrix, we have to find the components analogous to a protein that lowers the transition state and energy barrier for optimal energy conversion. Axiomatic design helps to tune the J-aggregate overlap, engineering the barrier less mixing of a charge transfer state into the exciton state and finally stabilize the charge separation against the back reaction(Figure 5.4).[15-17] On a conceptual level, the strategy behind the design is to choose a specific building block, which has a typical stacking to generate the topology of a

specific target *i.e.* reaction center or it could be a retro synthetic approach in which a specific target is reduced to functional entities which can self-assemble. Bichromophoric D1A2, light harvesting antenna with centrosymmetric dimers of perylene motif, could be further optimised as an antenna but also can be considered as the first step on the way to a reaction centre using the axiomatic design strategy. This approach is similar to how nature has done through evolution. These results enable a direct molecular level approach to axiomatic design and improvement of light harvesting antenna systems D1A2 with D1 and A2 as molecular entities. This will allow the designer to choose materials with predetermined structures to develop a nano-architecture of interest. Transfer of energy from donor to acceptor is achieved through FRET.[18] A water oxidation catalyst could be attached to perylene to design it as a half-cell for solar fuel device. Rich functionalities will help to tune the energy gap for optimum water oxidation and to harvest an extensive range of photons(Figure 5.5).

For the self-assembled structures of DATZnS(3'-NMe), the challenge is to guide the design of planar two-dimensional salphen-NDI based supramolecular frameworks containing chromophores with a recognition motif to establish a device capable of doing effective charge separation with PCET for driving water oxidation catalysts.[19] Knowledge about the orientation of the DATZnS(3′-NMe) on the surface of the grid helps to design the electrode for solar fuel cell device. The catalyst could be attached at the zinc salphen, which has Lewis acid character.[1] A grid formed from the alignment of the electric dipole and NDI stacks gives a strong scaffold to attach the catalyst. The supramolecular scaffold with well-defined building units opens the possibility of modifying it as a nanorod. Electronegative bromine on the 4, 5 carbon atoms make it suitable for a selective nucleophilic substitution of anchoring groups like carboxyl, to attach to the electrode surface. It could be possible to modify the terminal methyl group of the alkyl chain to attach to the electrode surface. The flexibility of the molecule is the added advantage to modify it according to the need of a solar fuel cell device.

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