“Supramolecular Architectures for Artificial Photosynthesis”

Monday 20th May
14:00-15:00
Lecture Theatre 4

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ABSTRACT: All of Earth’s oxygen is the result of water oxidation performed by photosynthetic organisms using solar light as the only energy source. The O₂ necessary for our aerobic life is produced by the photocatalytic cleavage of the extremely stable H-O-H bonds. Making oxygen is exceptionally difficult and lethal for any biological factory, which calls out a continuous self-repair cycle during oxygenic photosynthesis. Indeed, and despite the vast bio-diversity footprint, just one specialized protein complex is used by Nature as the H₂O-photolyzer: photosystem II (PSII). Man-made systems are still far from replicating the complexity of PSII. High resolution imaging of the PSII “core” complex shows the ideal co-localization of multi-chromophore Light Harvesting antennas with the functional Reaction Center (LH-RC). Our results overcome the classical “photo-dyad” model, based on a donor-acceptor binary combination. Here we report the self-assembly of multi-perylenebisimide chromophores (PBI) shaped to function by interaction with a polyoxometalate water oxidation catalyst (Ru₄POM). The resulting [PBI]₅Ru₄POM complex is identified as the minimal photosynthetic unit, formed both in solution and on photoelectrodes, showing: (i) a red-shifted, light harvesting efficiency (LHE>40%), (ii) favorable exciton accumulation and negligible excimeric loss; (iii) a robust amphiphilic structure; (iv) dynamic aggregation into large 2D-paracrystalline domains. Our results include the X-ray diffraction analysis of a dense, quasi-hexagonal packing of the functional motif, showing a striking analogy with the coexistence of fluid-to-crystalline phases in the native photosynthetic membrane. Photoexcitation of the PBI-antenna triggers one of the highest driving force for photo-induced electron transfer applied so far. The modularity of the building blocks, the simplicity of the non-covalent chemistry and the biomimetic appeal of the supramolecular approach, offer a unique opportunity for innovation in Artificial Photosynthesis.

BIOGRAPHY: Marcella Bonchio is Full Professor of Organic Chemistry at the University of Padova. She received the PhD degree in Physical Organic Chemistry in 1993, learning from her first Italian “maestri”: Giorgio Modena and Fulvio Di Furia, and later on with John O. Edwards at Brown University, and with Jay Groves at Princeton University in the USA. Marcella Bonchio has published > 140 papers in international journals, with > 6000 citations (h-index of 45). She has received the National Price for Research Innovation in 2011 and she is involved in National and EU-funded projects dealing with molecular systems for artificial photosynthesis. Her research interests focus on bio-inspired catalytic processes, nano-materials and reaction mechanisms emerging from the interplay of active metal cores and the surrounding environment. A recent breakthrough deals with the design of new organic-inorganic nano-systems enabling water splitting upon ultra-fast, photoinduced electron-transfer.