

Tuesday, 15th November, 12.00pm

Seminar Room

Host: Prof. Luis M. Liz-Marzán

Supramolecular Architectures for Artificial Photosynthesis: The Quantasome Vision

Marcella Bonchio

University of Padova and ITM-CNR, INSTM unit of Padova,
Department of Chemical Sciences, via Marzolo 1, Padova I-35131, Italy,
(marcella.bonchio@unipd.it)

<https://nanomolcat.wixsite.com/nanomolcat>

In the early studies, on Oxygenic Photosynthesis, the “quantasome hypothesis” led to seminal discoveries correlating the structure of natural photosystems with their complementary photo-redox functions.[1,2] Indeed, and despite the vast bio-diversity footprint, just one 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, showing the ideal co-localization of Light Harvesting antennas with the functional Reaction Center (LH-RC). Here we report the design of multi-perylenebisimide (PBI) networks shaped to function by interaction with a polyoxometalate water oxidation catalyst (Ru₄POM).[3-5] Our results point to overcome the classical “photo-dyad” model, based on a donor-acceptor binary combination, with integrated artificial “quantasomes” formed both in solution and on photoelectrodes, showing a: (i) 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.[5] Photoexcitation of the PBI-quantasome triggers one of the highest driving force for photo-induced electron transfer applied so far.[5-7]

References

- [1] Scheuring, S., Sturgis, J. N. *Chromatic Adaptation of Photosynthetic Membranes*. *Science* 309, 484–487 (2005);
- [2] Sartorel, A., Carraro, M., Toma, F. M., Prato, M., Bonchio, M. *Shaping the beating heart of artificial photosynthesis: oxygenic metal oxide nano-clusters*. *Energy Environ. Sci.* 5, 5592 (2012);
- [3] Piccinin, S.; Sartorel, A.; Aquilanti, G.; Goldoni, A.; Bonchio, M.; Fabris, S. *Water oxidation surface mechanisms replicated by a totally inorganic tetraruthenium-oxo molecular complex*. *Proc. Natl. Acad. Sci.* 110, 4917–4922 (2013)
- [4] Toma, F. M.; Prato, M.; Bonchio, M. et al. *Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces*. *Nature Chemistry* 2, 826-831 (2010).
- [5] Bonchio, M.; Sartorel, A.; Prato, M. et al. *Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation*. *Nature Chemistry* 11, 146-153 (2019).
- [6] Gobbo, P.; Bonchio, M.; Mann, S. et al. *Catalytic processing in ruthenium-based polyoxometalate coacervate protocells*. *Nature Commun* 11, 41 (2020).
- [7] Gobbato T.; Rigodanza F.; Benazzi, E.; Prato, M.; Bonchio M. et al. *J. Am. Chem. Soc.* 144, 14021-14025 (2022).