

# Exploring the Extent of Triplet State Delocalisation in Porphyrin Nanostructures

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Photoexcited triplet states play an important role in many photochemical mechanisms. Long known to be of paramount importance in the study of photosynthetic reaction centres, they have more recently also been shown to play a major role in a number of applications in the field of molecular electronics. Their characterisation is crucial for an improved understanding of the underlying processes with a particular focus on the determination of the spatial distribution of the triplet state wavefunction providing information on charge and energy transfer efficiencies.<sup>[1,2]</sup> Currently, active research in this field is mostly focussed on the investigation of materials for organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs).<sup>[3,4]</sup> Since the properties of triplet states and their spatial extent are known to have a major impact on device performance, a detailed understanding of the factors governing triplet state delocalisation is at the basis of the further development and improvement of these devices. In this contribution, we investigate triplet state delocalisation in a range of linear and cyclic Zn-porphyrin nanostructures (Figure 1) by transient electron paramagnetic resonance spectroscopy and discuss the factors governing the spatial extent of the triplet wavefunction.<sup>[5-7]</sup>

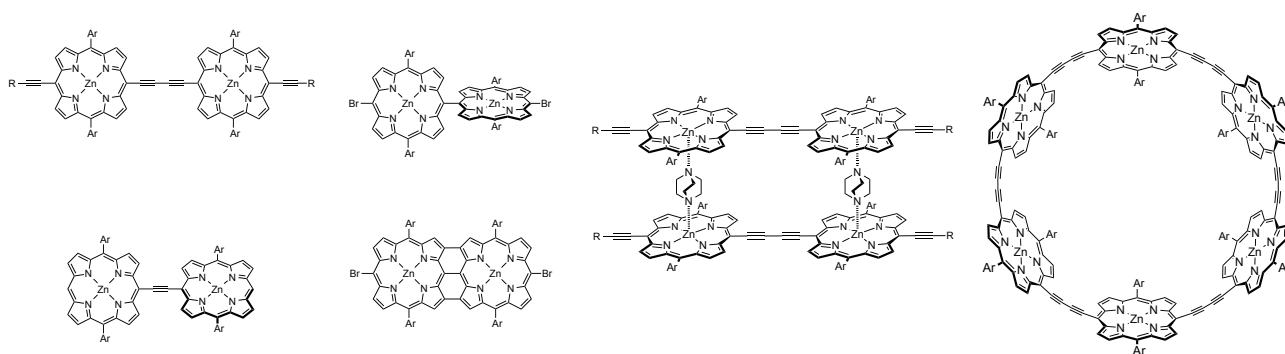


Figure 1: Selected examples of the investigated molecular structures.

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**References:**

- [1] C.E. Tait, P. Neuhaus, M.D. Peeks, H.L. Anderson, C.R. Timmel, *J. Am. Chem. Soc.*, **2015**, 137, 8284–8293.
- [2] P.J. Angiolillo, V.S.-Y. Lin, J.M. Vanderkooi, M.J. Therien, *J. Am. Chem. Soc.*, **1995**, 117, 12514–12527.
- [3] J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Köhler, R.H. Friend, *Nature*, **2001**, 413, 828–831.
- [4] A. Rao, P.C.Y. Chow, S. Gélinas, C.W. Schlenker, C.-Z. Li, H.-L. Yip, A.K.-Y. Jen, D.S. Ginger, R.H. Friend, *Nature*, **2013**, 500, 435–440.
- [5] S. Richert, M. Peeks, C.E. Tait, H.L. Anderson, C.R. Timmel, *Phys. Chem. Chem. Phys.*, **2016**, 18, 24171–24175.
- [6] S. Richert, G. Bullard, J. Rawson, P.J. Angiolillo, M.J. Therien, C.R. Timmel, *submitted for publication*.
- [7] S. Richert, B. Limburg, H.L. Anderson, C.R. Timmel, *unpublished*.