

## Energy transfer in bio-mimetic molecular nanorings

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Natural evolution very early on solved the problem of how to capture light efficiently and use it to initiate the primary electron transfer reactions of photosynthesis in a surprisingly efficient manner. Synthetic molecules that mimic such biological light-harvesting complexes should allow high-efficiency conversion of solar light into energy in the form of electrical current, rather than biological mass. We have investigated a family of synthetic porphyrin nanorings that mimic the ultrafast energy transfer and delocalization observed in natural light-harvesting systems such as LH2 in purple bacteria.  $\pi$ -Conjugated nanorings with diameters of up to 10 nm, consisting of up to 24 porphyrin units, are found to exhibit excitation delocalization within the first 200fs of light absorption [1,2]. Transitions from the first singlet excited state of the circular nanorings are dipole-forbidden as a result of symmetry constraints, but these selection rules can be lifted through static and dynamic distortions of the rings. For highly symmetric rings, the radiative rate is found to increase with increasing temperature [1]. As expected, the activation energy for emission increases when a nanoring is fixed in a circular conformation by coordination to a radial template. We further demonstrate that as the diameter of the nanorings increases beyond  $\sim 10$  nm, its electronic properties tend towards those of a similarly sized linear molecule, as a result of excitation localization on a sub-segment of the ring [2]. However, significant differences persist in the nature of the emitting dipole polarization even beyond this limit, arising from variations in molecular curvature and conformation. We have also investigated LH2-like supramolecular double- and triple-stranded complexes based upon porphyrin nanorings [3]. Energy transfer from the antenna dimers to the  $\pi$ -conjugated nanoring occurs on a subpicosecond time scale, rivaling transfer rates in natural light-harvesting systems. The presence of a second nanoring acceptor doubles the transfer rate, providing strong evidence for multidirectional energy funneling. These complexes are hence versatile synthetic models for natural light-harvesting systems.

[1] Yong, Parkinson, Kondratuk, Chen, Stannard, Summerfield, Sprafke, O'Sullivan, Beton, Anderson, and Herz, *Chemical Science* **6**, 181 (2015).

[2] Parkinson, Kondratuk, Menelaou, Gong, Anderson, and Herz, *J. Phys. Chem. Lett.* **5**, 4356 (2014).

[3] Parkinson, Knappke, Kamonsutthipaijit, Sirithip, Matichak, Anderson, and Herz, *J. Am. Chem. Soc.* **136**, 8217 (2014).