Molecular Photovoltaics, Switches, and Photonic Wires Based on Porphyrins and Fullerenes

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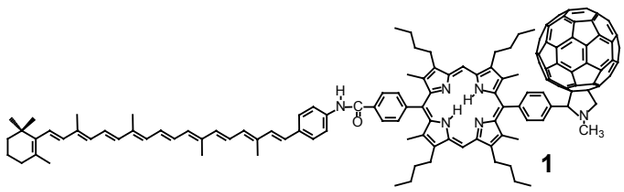
Biology is the best example of nanoscale technology. Photosynthesis provides paradigms for the design of synthetic molecules that carry out interesting photochemical processes and may lead to nanotechnological applications. For example, photosynthetic antennas are photonic "wires" and switches that move excitation energy spatially, and control its delivery to reaction centers. Reaction centers are molecular-scale photovoltaics that use light energy to initiate photoinduced electron transfer cascades leading to long-lived, energetic charge-separated states. The energy stored in these states is used to power nanoscale ion pumps and protein-based mechanical motors.

Ideas borrowed from photosynthesis can be used in the design of biomimetic molecules that carry out similar functions. For example, carotenoid-porphyrin-fullerene (C-P-C_{60}) triad **1** undergoes photoinduced electron transfer to form a high-energy charge-separated state $C^{\bullet+}$-P-$C_{60}^{\bullet-}$. Charge recombination yields either the ground state or the carotenoid triplet state. The charge recombination rate is sensitive to small magnetic fields, and **1** can exhibit a molecular AND logic gate function. In hexad **2**, the zinc porphyrin array acts as an antenna, absorbing light and transferring excitation energy to the free base porphyrin. Electron donation from the free base porphyrin to the fullerene then generates a charge-separated state. Triad **3** is a porphyrin-fullerene molecular photovoltaic whose function can be switched on or off by the attached photochromic dithienylethene moiety. In the open, colorless form, the dithienylethene has no effect on the photochemistry of the porphyrin, whose excited singlet state donates an electron to the fullerene. Ultraviolet irradiation converts the dithienylethene to the closed, colored form, which quenches the porphyrin excited singlet state by energy transfer, precluding significant electron transfer. The design and photochemistry of these and other biomimetic constructs will be discussed.



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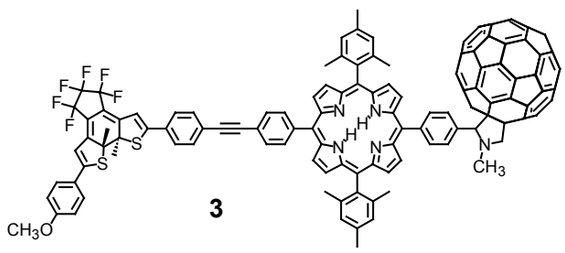

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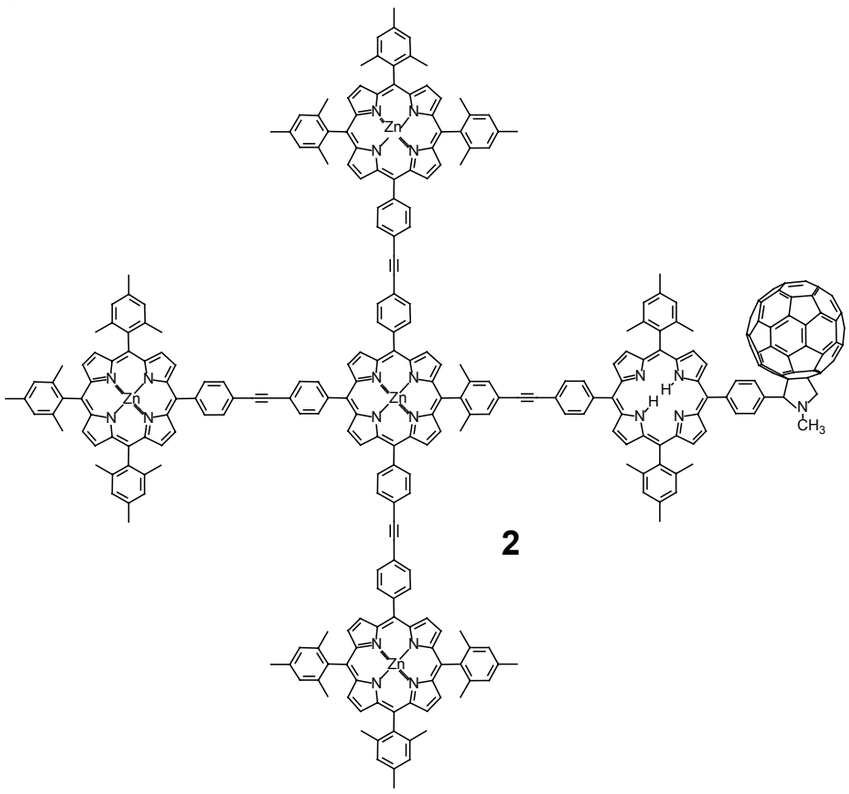

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