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A Molecular Photonic Wire

Richard W. Wagner and Jonathan S. Lindsey*

Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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A wire is a device that conveys a signal or permits the flow of energy. As such, in addition to its transmission capabilities, a wire must include provisions for connection to an input device on one end and an output device on the other. The increasing interest in molecular scale devices has focused attention on the synthesis of molecular wires.[1] The wires have been envisaged as carriers of electrons (or holes). With molecular electronic wires the "connection problem" of attaching macroscopic input and output devices remains a major challenge.

Our approach to molecular wires is inspired by the light-harvesting complexes in photosynthesis, which comprise hundreds of pigments in a solid-state array.[2] The excited state resulting from light absorption by one pigment migrates among the array of pigments, ultimately reaching a reaction center. We felt that an appropriate synthetic array of pigments could function as a molecular photonic wire. A molecular photonic wire is distinguished from a molecular electronic wire by supporting excited-state energy transfer rather than electron- (or hole-) transfer processes. The use of light to produce the excited state, as occurs in photosynthesis, provides a natural means of inputting a signal to a molecular wire. A fluorescent dye can be used to output an optical signal. The design of molecular photonic wires has much in common with the design of synthetic light-harvesting systems.[3,4]

The structure of the molecular photonic wire (**1**) is shown in Scheme 1. A boron-dipyrromethene dye provides an optical input at one end, a linear array of three zinc porphyrins is employed as a signal transmission element, and a free base porphyrin provides an optical output at the other end. The synthesis of **1** combines modular building blocks[5] in a stepwise manner using coupling reactions similar to those in our synthesis of multi-porphyrin light-harvesting arrays[3] (supplementary materials). The end-to-end distance of **1** is estimated to be 90 Å. **1** is highly soluble in toluene (>5 mM).

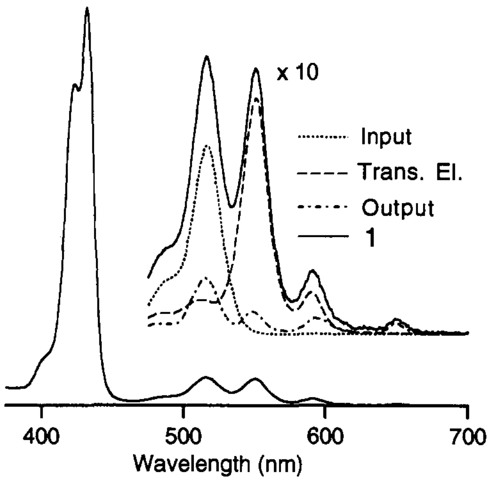

Figure 1. Absorption spectrum of **1** and its component parts[7] in toluene at room temperature.

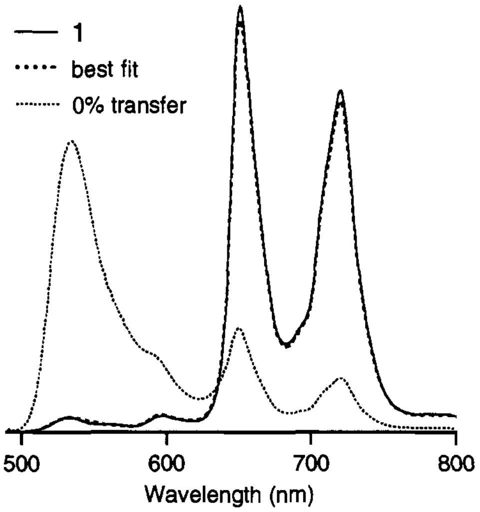

Figure 2. Fluorescence emission spectrum of **1** (λ_{ex} = 485 nm) in toluene at room temperature. Emission maxima: boron-dipyrromethene dye (534 nm), zinc porphyrin (597, 646 nm; 1:1.8 peak height ratio), free base porphyrin (650, 720 nm). A simulated spectrum is shown for 0% transfer at all four steps. The best fit occurs with stepwise transfer efficiencies of 95%, 93%, 93%, and 93%.

The absorption spectrum of **1** in toluene at room temperature is shown in Figure 1. The porphyrin Soret band ($\lambda \sim 420$ nm) is split. The absorption bands in the visible region (450-700 nm), however, closely match the sum of the component parts of the molecule.[6] With illumination at 485 nm the input dye absorbs 62% of the light, 12% is absorbed by the output dye, and 26% is absorbed by the three zinc porphyrins that constitute the transmission element.

Illumination of **1** at 485 nm results in the emission spectrum shown in Figure 2. The integrated fluorescence quantum yield (500-800 nm) of **1** is 0.107. Of this emission, 3% arises from the input dye, 5% leaks from the zinc porphyrins, and 92% is emitted by the free base porphyrin. The fluorescence of the input dye is quenched by 26-fold compared with a similarly-substituted boron-dipyrromethene model compound, a value consistent with 96% energy transfer to the neighboring zinc porphyrin. Illumination of **1** at 649 nm (where only the free base porphyrin absorbs) shows the free base porphyrin to have $\Phi_f = 0.121$, a value slightly greater than that of a monomeric free base porphyrin ($\Phi_f = 0.114$). The emission intensity of the free base porphyrin is 6.8 times higher than expected due to its absorption at 485 nm (12% of the total) and its known quantum yield. These results can only be explained by efficient energy transfer from the input dye and transmission element to the free base porphyrin at the other end of the molecule.

In order to extract the signal transmission efficiency from these results, we have simulated the emission spectrum of **1** using quantitative spectral data of the component parts[7] and various

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(6) The intensities of the (0-0) and (2-0) bands of the zinc porphyrin increase slightly upon incorporation into the linear array. Use of the absorption spectrum of the all-zinc porphyrin trimer gives a near-perfect match with the absorption spectrum of **1**.

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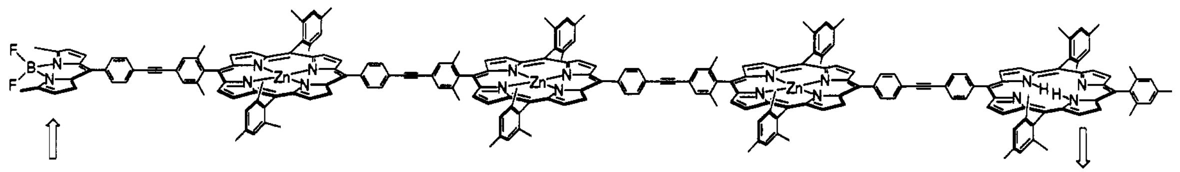
Scheme 1



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values of the individual energy-transfer steps. The spectrum resulting from the extreme case of 0% energy transfer at all steps (five non-interacting chromophores) is shown in Figure 2. A near-perfect match with the data is observed for stepwise transfer efficiencies of 95%, 93%, 93%, and 93% in proceeding from input to output (Figure 2).[8] On the basis of these values, the overall signal transmission efficiency from input to output is 76%.

The high yield of energy transfer, the relatively unaltered visible absorption spectra, and the absence of significant electron-transfer quenching in this multichromophoric system are remarkable. One treatment of the signal transmission process involves Forster-type stepwise energy transfer among the chromophores. The expected Forster transfer efficiencies are 93%, 28%, 28%, and 77%, giving an overall transmission efficiency of <6% from input to output. The observed efficiency is 13 times higher, indicating that energy transfer is mediated by the diarylethyne linker. It is noteworthy that the expected Forster transfer efficiency for through-space transfer from input to output (bypassing the three zinc porphyrins) is 0.1%, a negligible contribution to the observed spectrum.[9] The mechanism of energy transfer and the extent of electronic communication in these types of arrays are currently under investigation.[10]

Devices must meet a stringent set of criteria for computational applications.[11] Still, if future molecular-scale information processing systems are to be built around photochemical switches,[12] gates,[13] and memory devices,[14] molecular photonic wires could be useful for signal transmission among these molecular devices. The performance of molecular photonic wires can be refined by using light-harvesting arrays as input chromophores, tuning the molecular architecture and photophysical parameters to achieve higher signal transmission efficiencies, and using brighter output dyes. Light has distinct advantages for communicating with molecular devices. Molecular photonic wires absorb an optical signal, enable facile excited-state energy migration, and emit an optical signal at a distant site. Questions such as "How far can excited-state energy be transmitted?" and "Can this form of photonic signal transmission be gated?" are preeminent. The molecular design and building block approach we have developed should enable synthesis of more elaborate devices where these and related issues can be addressed.

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Supplementary Material Available: Experimental details for the synthesis and characterization of **1** including SEC, ^{1}H NMR, mass, absorption, and emission spectral data (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(7) Quantitative spectral data were obtained from model compounds bearing ethynyl groups, including a boron–dipyrromethene dye (input, $\Phi_f = 0.108$), an all-zinc porphyrin trimer (transmission element, $\Phi_f = 0.037$), and a free base porphyrin (output, $\Phi_f = 0.114$). Quantum yields were determined by ratioing to Rhodamine 123 (0.90), ZnTPP (0.030), or TPP (0.11), respectively.

(8) This analysis is overparametrized as the emission spectra of the three zinc porphyrins are indistinguishable. An equivalent result is obtained with a three-component simulation using transfer efficiencies of 95% (input to all-zinc porphyrin trimer) and 80% (all-zinc porphyrin trimer to free base porphyrin). A deviation of ±1% in either value gives a poorer fit.

(9) This Forster calculation assumes free rotation about the ethyne bond, a rigidly collinear array of chromophores, and is based on center-to-center distances. Ethynes bend easily,[9a,b] but our measurements[9c] on similar arrays indicate that the average deformation of adjacent porphyrin in-plane axes is ~16 Å. (a) Montgomery, L. K.; Applegate, L. E. *J. Am. Chem. Soc.* **1967**, *89*, 2952–2960. (b) Allinger, N. L.; Pathiaseril, A. *J. Comput. Chem.* **1987**, *8*, 1225–1231. (c) Bothner-By, A. A.; Dadok, J.; Johnson, T. E.; Lindsey, J. S. Manuscript in preparation.

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