Molecular Optoelectronic Gates

Richard W. Wagner,[†] Jonathan S. Lindsey,*[,†] Jyoti Seth,[‡]
Vaithianathan Palaniappan,[‡] and David F. Bocian*[,‡]

Department of Chemistry
Carnegie Mellon University, 4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213-2683
Department of Chemistry, University of California
Riverside, California 92521-0403

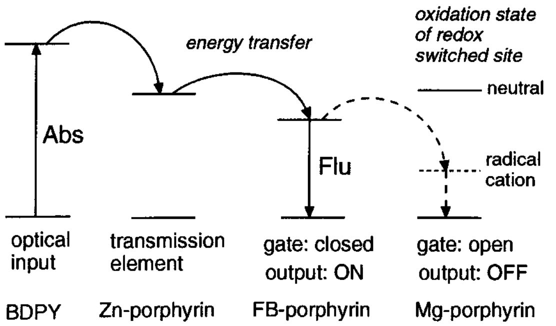
Received January 25, 1996

The development of molecular-scale information-processing systems requires the creation of molecular devices which function as wires, gates, memory elements, sensors, and related components. We recently developed a molecular photonic wire consisting of an array of pigments 90 Å in length.[1] Absorption of a photon of visible light by an input chromophore at one end of the array leads to emission of a photon by an output chromophore at the opposite end of the array. The quantum yield of energy migration from input to output is estimated to be 76%. We sought to develop methods for gating the signal transmission in this type of wire, thus allowing the emission at the output to be turned on/off in a controlled manner. If a channel funneling energy to the ground state could be opened selectively on one pigment strategically placed on the wire, this would cause quenching of the excited state and thereby give no fluorescence output. In this paper we describe molecular devices where an electronic energy transfer process is selectively gated by one-electron alteration of the redox state of one spatially isolated pigment in a multipigment array.

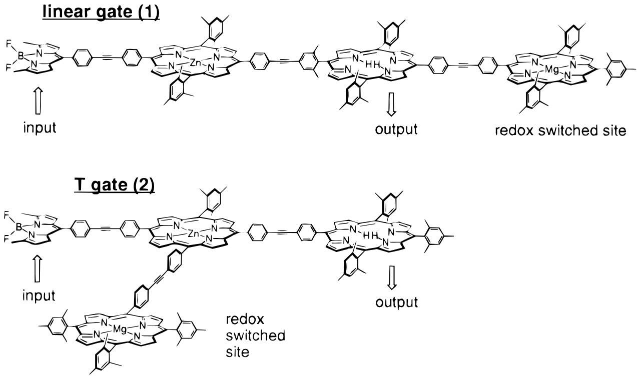
Many metalloporphyrins undergo reversible oxidation yielding stable radical cations,[2] and these radical cations are generally nonfluorescent due to their low-lying excited states.[3] This combination of redox and photochemical phenomena makes metalloporphyrins ideal for incorporation as the switching element in an optical device whose output can be turned off/on by oxidation and reduction, respectively, and in principle can be achieved by chemical, electrochemical, or photochemical means. To serve as the redox switch, a particular metalloporphyrin must satisfy four design criteria: (1) In the neutral state, the metalloporphyrin should have a higher energy absorption than that of the free base porphyrin so that energy transfer does not occur from free base to metalloporphyrin. (2) In the oxidized state, the metalloporphyrin should have low-lying energy levels and exhibit no fluorescence upon excitation. (3) The metalloporphyrin should exhibit reversible redox properties. (4) The metalloporphyrin should have the highest energy highest occupied molecular orbital (HOMO) of all the pigments in the array. The last requirement ensures that oxidation will take place selectively at the designated site.

In the design of the molecular wire, the input chromophore is a boron−dipyrromethene dye (BDPY),[4] the transmission element consists of three Zn-porphyrins, and the output chromophore is a free base (FB) porphyrin. To create an optoelectronic gate based on this design, we have incorporated a Mg-porphyrin as the redox switch, as the ease of oxidation follows the series Mg > Zn > FB-porphyrins. Furthermore, the absorption bands of a Mg-porphyrin radical cation extend into the near-IR (>1000 nm), indicative of a manifold of low-lying singlet excited states.[2] This manifold includes very low-energy states (~3000 cm^{-1}) arising from configurations wherein an electron is promoted from the filled HOMO-1 to the half-filled HOMO of the radical cation. This design strategy is illustrated in Chart 1.

Chart 1. Schematic Diagram of Excited-State Energy Levels of Pigments in the Arrays



Scheme 1. Structures of Linear Gate (**1**) and T-Gate (**2**)



The two gates we have developed to test the ideas delineated above are shown in Scheme 1. One gate is linear in design (**1**) and has the redox switch (the Mg-porphyrin) attached to the terminus of the array, while the other is a T-shaped gate (**2**) with the switch attached to the Zn-porphyrin. In the linear gate, oxidation of the switch must cause quenching of the output chromophore (FB-porphyrin). In the T-gate, oxidation must deactivate the excitation as it passes through the transmission element (Zn-porphyrin).

The syntheses of the gates employ porphyrin building blocks[5] in defined metalation states (FB, Zn, or Mg[6]) that are joined under mild Pd-mediated reactions.[7] The gates **1** and **2** dissolve readily in a variety of organic solvents. As for the molecular wire, the visible absorption spectrum of both **1** and **2** is the sum of the component parts. For each of the neutral gates, excitation at 485 nm, where the boron−dipyrromethene dye absorbs 69% of the light, yields fluorescence emission predominantly from the FB-porphyrin. The quantum efficiency of energy migration from input to output in each case is >80%.

Upon treatment of a solution of either gate (**1** or **2**) in CH_2Cl_2−ethanol (9:1) with an excess of a chemical oxidant such as $Fe(ClO_4)_3$, the fluorescence emission of the FB-porphyrin markedly decreases (Figure 1).[8] The optical spectrum of the

---

[†] Carnegie Mellon University.

[‡] University of California.

(1) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760.

(2) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, pp 53−126.

(3) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. III, pp 1−165.

(4) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.*, in press.

(5) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941−8968. Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440.

(6) Lindsey, J. S.; Woodford, J. N. *Inorg. Chem.* **1995**, *34*, 1063−1069.

(7) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266−5273.

(8) The determination of the magnitude of the fluorescence decline is limited by residual fluorescence from molecules that have undergone demetalation of magnesium during the oxidation process. The amount of demetalation depends on the solvent and oxidant. Electrochemical oxidation in $CHCl_3$:CH_2Cl_2 (3:1) gives about 3% demetalation of the Mg-porphyrin

0002-7863/96/1518-3996$12.00/0

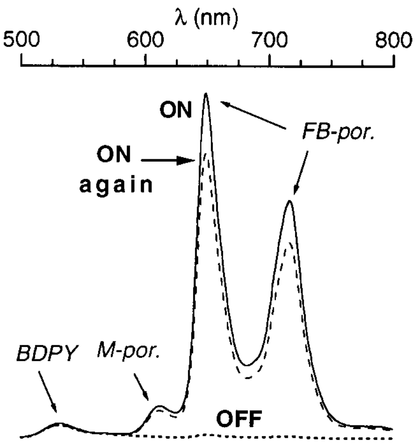


Figure 1. Fluorescence spectrum of gate **2** in CH_2Cl_2:ethanol (9:1) before (ON) and after (OFF) oxidation and upon reduction with triethylamine (ON again).

oxidized gate shows absorption bands exclusively due to the boron−dipyrromethene dye, the Zn- and FB-porphyrins, and the oxidized Mg-porphyrin. The addition of triethylamine causes reduction of the Mg-porphyrin radical cation, recovery of the neutral compound, and 83−95% recovery of the fluorescence signal. Similar recoveries were obtained electrochemically. To ensure that the use of excess chemical oxidant does not cause oxidation of pigments other than the Mg-porphyrin, quantitative spectroelectrochemistry also was performed.

The electrochemistry of the gates was done in $CHCl_3$:CH_2Cl_2 (3:1). The $E_{1/2}(1)$ value for the Mg-porphyrin is 0.34 V (vs Ag/Ag^+).[9] The $E_{1/2}(1)$ values for the Zn and FB-porphyrins and $E_{1/2}(2)$ for the Mg-porphyrin appear as a broad wave near 0.72 V and are not resolved. The $E_{1/2}(2)$ for the Zn-porphyrin is at 0.91 V. The difference in potentials between the Zn- and Mg-porphyrins (~300−380 mV) is sufficient to enable highly selective oxidation of the Mg-porphyrin (>99.9%) with minimal oxidation of the Zn-porphyrin (<4%).[10] The bulk electrolysis of **1** was carried out at 0.54 V, a potential ensuring 99.9% oxidation of the Mg-porphyrin, and the fluorescence was scanned with the compound under this potential. The residual fluorescence in the oxidized species observed upon illumination at 488 nm is 4% at 650 nm (where both the Zn- and FB-porphyrins emit) and 3% at 718 nm (where only the FB-porphyrin emits). These results indicate that oxidation of the Mg-porphyrin in **1** causes a 33-fold decrease in fluorescence emission from the output chromophore of the gate.[8]

In previous experiments on partially oxidized multiporphyrin arrays composed of Zn-porphyrins, facile intramolecular hole-hopping among isoenergetic porphyrins was observed.[11] In **1** and **2**, hole-hopping does not occur (as determined by EPR spectroscopy) because the redox potential of the Mg-porphyrin is several hundred millivolts lower than that of the other porphyrin components of the gate. We attribute the facile quenching of the excited state (the FB-porphyrin in **1**, the Zn-porphyrin in **2**) to an energy transfer process that leads to excitation deactivation through the Mg-porphyrin radical cation which has the lowest energy excited states in the gate. Energy transfer to this component results in rapid dissipation of the excited-state energy and irreversible relaxation to the ground state. Transient optical experiments are required to confirm this hypothesis and to rule out the alternative possibility of electron transfer as an excited-state quenching process.

In summary, we have demonstrated gating of a photonic signal in a molecular device via a spatially isolated redox switch. This gating process can be used for wires that involve energy migration as the basis for signal transmission, is particularly attractive as it does not involve changes in molecular conformation, and in principle also can be achieved by photochemical means. These molecular gates complement molecular sensors or switches where the luminescent readout of one chromophore is altered by conformational changes or the availability of photoinduced electron transfer processes to an adjacent site.[12] Access to these gates is made possible by a modular approach that enables incorporation of a wide variety of metalloporphyrin building blocks with desired redox and photophysical properties. We anticipate that these types of gates could be used to transmit signals across lipid bilayers and other interfaces, could provide the basis for various types of sensors, and may be useful in future molecular-scale information-processing systems.

Acknowledgment. The development of the porphyrin building block approach was supported by NIH Grant GM36238 (J.S.L.). The spectroelectrochemical measurements were supported by NIH Grant GM36243 (D.F.B.) and a grant from the LACOR program sponsored by Los Alamos National Laboratory (D.F.B.).

JA9602657

(yielding a neutral FB-porphyrin) in the linear gate, while chemical oxidation with $Fe(ClO_4)_3$ in CH_2Cl_2:ethanol (9:1) gives no detectable demetalation.

(9) The $E_{1/2}$ values were measured vs Ag/Ag^+ (scan rate 0.1 V/s; $E_{1/2}$ of ferrocene/ferrocenium = 0.22 V) in $CHCl_3$:CH_2Cl_2 (3:1) containing 0.1 M $(n\text{-Bu})_4NPF_6$.

(10) In neat CH_2Cl_2 the Zn-porphyrin oxidation wave is at ~0.62 V, while in $CHCl_3$:CH_2Cl_2 (3:1) the center of the broad wave for the Zn- and FB-porphyrins is at 0.72 V. The shift in the Zn-porphyrin wave is conservatively estimated to be <20 mV on the basis of studies of monomers; hence, the estimate of 4% oxidation of the Zn-porphyrin is an upper bound under conditions which produce >99.9% Mg-porphyrin oxidation.

(11) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578−10592.

(12) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, 197−202. Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; Sandanayake, K. R. A. S. *Chem. Soc. Rev.* **1992**, 187−195. Knorr, A.; Daub, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2664−2666. Goulle, V.; Harriman, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1034−1036. Huck, N. P. M.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1095−1096.