

Design and Synthesis of Porphyrin-Based Optoelectronic Gates

Arounaguiry Ambroise,[§] Richard W. Wagner,[§] Poliseti Dharma Rao,[§]
Jennifer A. Riggs,[§] Philippe Hascoat,[§] James R. Diers,[†] Jyoti Seth,[†]
Robin K. Lammi,[‡] David F. Bocian,[†] Dewey Holten,[‡] and Jonathan S. Lindsey*[§]

Department of Chemistry, University of California, Riverside, California 92521-0403,
Department of Chemistry, Washington University, St. Louis, Missouri 63130-4889, and
Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27695-8204

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Two porphyrin-based optoelectronic gates and several prototypical redox-switching components of gates have been synthesized for studies in molecular photonics. Linear and T-shaped molecular optoelectronic gates contain a boron-dipyrin (BDPY) dye as the input unit, a zinc (Zn) porphyrin as the transmission unit, a free base (Fb) porphyrin as the output unit, and a magnesium (Mg) porphyrin as the redox-switching unit. The linear gate and T gate were synthesized using a molecular building block approach. In the linear gate synthesis, a BDPY–Zn porphyrin dyad was coupled with a Fb porphyrin–Mg porphyrin dimer. The synthesis of the T gate utilized a Zn porphyrin bearing four different meso substituents: mesityl, 4-iodophenyl, 4-[2-(trimethylsilyl)ethynyl]phenyl, and 4-[2-triisopropyl]ethynyl]phenyl. Attachment of the three different groups to the Zn porphyrin was accomplished using successive Pd-mediated coupling reactions in the following sequence: Fb porphyrin (output unit), BDPY dye (input unit), and Mg porphyrin (redox-switching unit). Both the linear gate and T gate syntheses introduce the Mg porphyrin at the final step to minimize demetalation of the Mg porphyrin. Refinements to various components of these gates were investigated through the preparation of a ferrocene–porphyrin, a ferrocene–phthalocyanine, and a ferrocene–porphyrin–phthalocyanine. A dyad motif for studies of optically based redox switching was prepared that contains a derivative of Ru(bpy)₃X₂ coupled to a porphyrin. From these and related studies have emerged a number of design considerations for the development of refined optoelectronic gates.

Introduction

The development of molecular-scale information processing systems requires a variety of molecular devices, including wires, switches, logic elements, memory elements, and input/output components. As a first step in our research program toward realization of a functional molecular device, we developed a molecular photonic wire.¹ The wire is shown in Chart 1 and is composed of a BDPY dye, three Zn porphyrins, and a Fb porphyrin. Excitation of the BDPY unit results in excited-state energy transfer followed by fluorescence from the Fb porphyrin. We subsequently sought designs that would enable the flow of excited-state energy and/or the fluorescence output in the molecular wire to be switched off/on in a reversible manner.

We elected to investigate oxidation/reduction as a means of controlling the excited-state energy-migration process in the molecular wire. The addition of a redox-switching unit to the wire affords an optoelectronic gate

(Figure 1). The attractions of a redox-switching unit include the absence of moving parts (other than electron transfer) and the prospect that the molecular architecture could be tethered to an electroactive surface and switched without involving molecular diffusion processes. In contrast, the vast majority of molecular switches designed to date employ conformational^{2–6} or diffusive motion⁷ as their basis of action. Though a variety of switches have been designed that employ redox changes as a means of altering the fluorescence

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* To whom correspondence should be addressed. E-mail: jlindsey@ncsu.edu.

[†] University of California.

[‡] Washington University.

[§] North Carolina State University.

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Chart 1

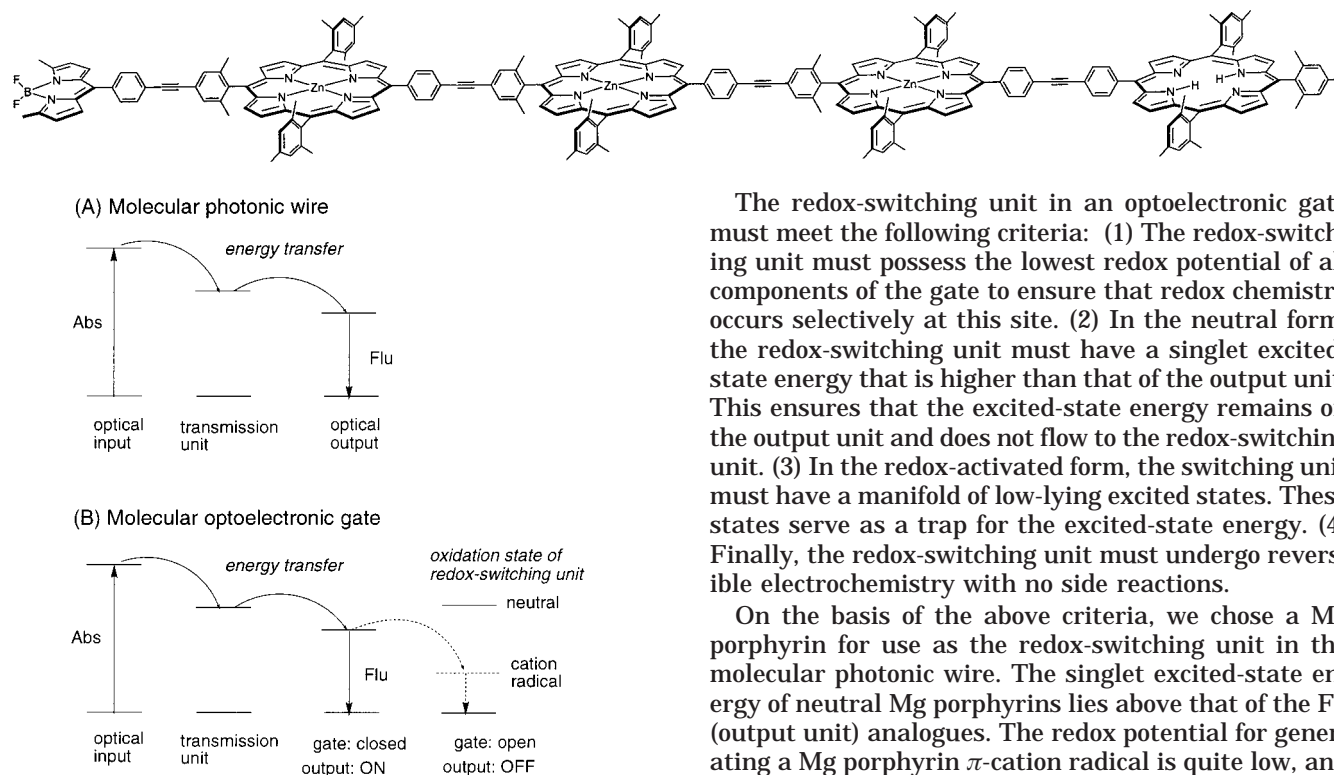


Figure 1. (A) Energy flow in a molecular photonic wire. (B) Energy flow in a molecular optoelectronic gate.

of an appended luminophore or the conductivity of an electronic wire,⁸ few switches have been developed that employ redox control over an excited-state energy-transfer process. One close analogy to our design (albeit still requiring diffusion) is a molecular photonic wire in which binding/liberation of a redox-active analyte causes suppression/enhancement of signal transmission and fluorescence.⁹ One notable example of a redox-based switch that lacks any moving parts is built around a molecule composed of two one-electron donors attached to a single two-electron acceptor. Optical excitation of the donors results in spectral changes upon transfer of one or two electrons to the acceptor. This system functions as an all-optical intensity-dependent photochromic switch.¹⁰

The redox-switching unit in an optoelectronic gate must meet the following criteria: (1) The redox-switching unit must possess the lowest redox potential of all components of the gate to ensure that redox chemistry occurs selectively at this site. (2) In the neutral form, the redox-switching unit must have a singlet excited-state energy that is higher than that of the output unit. This ensures that the excited-state energy remains on the output unit and does not flow to the redox-switching unit. (3) In the redox-activated form, the switching unit must have a manifold of low-lying excited states. These states serve as a trap for the excited-state energy. (4) Finally, the redox-switching unit must undergo reversible electrochemistry with no side reactions.

On the basis of the above criteria, we chose a Mg porphyrin for use as the redox-switching unit in the molecular photonic wire. The singlet excited-state energy of neutral Mg porphyrins lies above that of the Fb (output unit) analogues. The redox potential for generating a Mg porphyrin π -cation radical is quite low, and considerably lower than that of any of the other porphyrins in the molecular wire.¹¹ Porphyrin π -cation radicals in general exhibit an extensive manifold of low-lying excited states, as evidenced by their weak absorption spectra that extend into the near-IR region.¹² Porphyrin π -cation radicals are also relatively stable and can undergo facile reduction back to the neutral state. (The absorption spectrum of the cation radical of magnesium tetramesitylporphyrin as well as the spectrum of the porphyrin formed upon reduction of the cation radical with triethylamine are shown in the Supporting Information.) Collectively, these considerations led to two different designs, the T gate and the linear gate (Chart 2).¹³ In the T gate, the Mg porphyrin is attached to the transmission unit, while in the linear gate the Mg porphyrin is attached to the output unit.

The T gate and linear gate were anticipated to function in quite different ways. In the T gate, the redox-switching unit was anticipated to function by intercepting the excited-state energy prior to passage to the output unit. The operation of the T gate was anticipated to be quite demanding, as the residence time of the excited state at the Zn porphyrin was likely to be ≈ 20 ps (based on similar Zn porphyrin–Fb porphyrin dimers).¹⁴ In the linear gate, the redox-switching unit was required only to quench the excited state of the output unit. This process should be facile given that the excited state of the Fb porphyrin output unit exhibits a lifetime of ≈ 10 ns.

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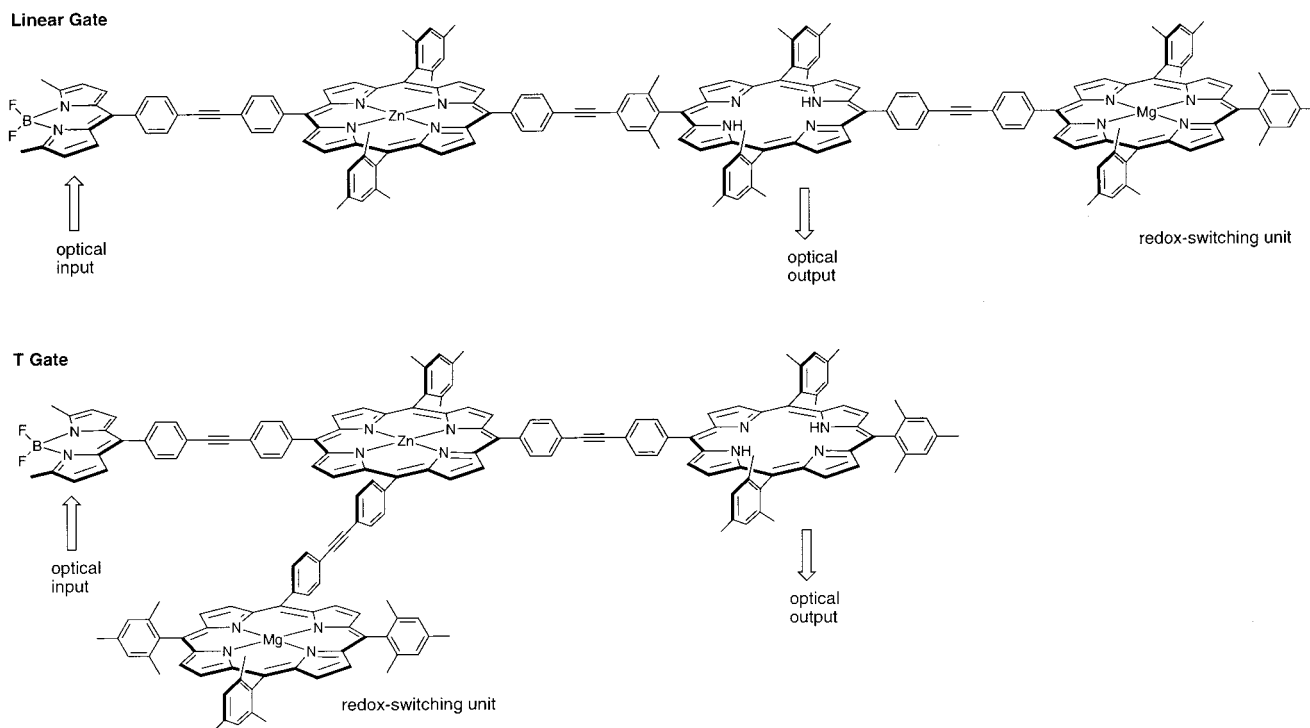
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Chart 2



Recently, we studied the dynamics of the energy-transfer processes in the linear- and T-shaped optoelectronic gates and their component parts.^{15–17} These studies have elucidated the dynamics and mechanism of energy flow in the gates, both of which are more complex than we originally anticipated: (1) Energy transfer occurs very rapidly ($k_{\text{trans}} = (9 \text{ ps})^{-1}$) from a Zn porphyrin to a Mg porphyrin joined via a diphenylethyne linker.¹⁵ Accordingly, the majority of the energy in the T gate initially flows to the site of switching rather than to the output unit. (2) Electronic communication in diphenylethyne-linked multiporphyrin arrays can proceed via superexchange among distant sites, such as from a Mg porphyrin to a Fb porphyrin in an array of Mg, Zn, and Fb porphyrins (i.e., like the T gate).¹⁶ Thus, in the T gate, the excited-state energy that initially reaches the Mg porphyrin then proceeds to the Fb porphyrin via superexchange. Qualitatively similar superexchange processes also occur between nonadjacent neutral and π -cation radical porphyrins in multiporphyrin arrays.¹⁷ This process makes quenching of the excited Fb porphyrin by the distant, oxidized Mg porphyrin essentially as effective as the quenching between these adjacent sites in the oxidized linear gate.

Recently, we sought to make a series of refinements to the molecular optoelectronic gates. (1) We wanted to use a much brighter far-red emitter as an output unit. This led to the investigation of phthalocyanines for the output unit. These molecules have much larger quantum yields of emission than do porphyrins. (2) We sought to employ a redox-switching unit that was less

labile than a Mg porphyrin. Thus, we investigated the use of ferrocene as a redox-switching unit. Ferrocene undergoes reversible electrochemistry and does not absorb substantially in the visible region. (3) We sought to employ a chromophore that could undergo a photo-induced internal charge-transfer process, thereby serving the same function as the redox-switching unit. This latter modification would provide the basis for the development of an all-optical gate. In this paper we describe the synthesis of the linear gate, T gate, and the modified prototypical redox-switching units. We also characterize the electrochemical and spectroscopic properties of the prototypical redox-switching units.

Results and Discussion

The linear gate and T gate both incorporate a BDPY dye, Zn porphyrin, Fb porphyrin, and a Mg porphyrin. We have previously prepared arrays composed of multiple BDPY dyes and one porphyrin,¹⁸ multiple Mg porphyrins and one Fb porphyrin,¹⁹ and multiple Zn porphyrins and one Fb porphyrin.^{19,20} Some of the constraints in preparing the linear and T gates have emerged from these prior syntheses. For example, the BDPY dyes are stable to the Pd-coupling conditions and are generally quite robust, but are susceptible to nucleophilic reagents such as fluoride used for deprotection of the trimethylsilylethyne functionality. While the Zn porphyrins and Fb porphyrins are readily handled with current methods for preparing multiporphyrin arrays, Mg porphyrins present two challenges. First, Mg por-

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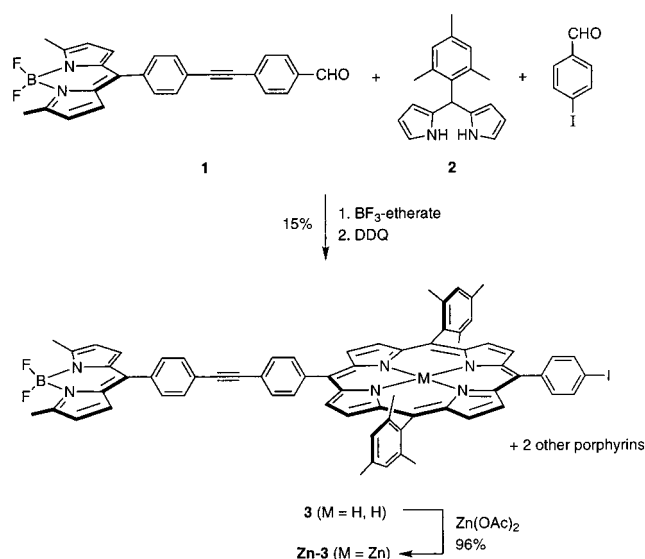
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Scheme 1



phyrins are readily demetalated by weak acids or silica gel.²¹ Second, Mg porphyrins are somewhat polar and tend to streak upon adsorption chromatography; this problem becomes more acute with multiporphyrin arrays containing one or more Mg porphyrins. Fortunately, the Mg porphyrin building blocks are stable to the Pd-coupling conditions and the trimethylsilylethyne deprotection conditions, both of which employ neutral to basic conditions.²² These constraints led to the synthetic routes employed.

I. Synthesis of the Linear Gate and T Gate

Linear Gate. The linear gate contains the following components in a linear sequence: BDPY dye, Zn porphyrin, Fb porphyrin, Mg porphyrin. A linear synthesis beginning with the Mg porphyrin switching unit would require multiple chromatography operations, and would need to be done without altering the metalation state of the Mg porphyrin.²³ Alternatively, a stepwise synthesis of the linear gate beginning with the BDPY unit was not viewed as practical due to the susceptibility of the BDPY unit to attack by the nucleophilic TBAF.²⁴ We therefore outlined a synthetic route that involved the preparation of a BDPY-porphyrin dyad (Scheme 1) and a Mg-Fb porphyrin dimer (Scheme 2), which are then joined to give the desired linear gate. This route had the following advantages: (1) requires four synthetic steps as compared to a stepwise route that would have involved six synthetic steps (three Pd-coupling reactions, three trimethylsilylethyne deprotection reactions) and (2) minimizes the synthetic and chromatography operations involving both the Mg porphyrin and the BDPY unit.

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(23) The five-component linear molecular wire was prepared in a stepwise manner beginning with the output chromophore (the Fb porphyrin) and proceeding through to the attachment of the input chromophore (the BDPY dye).¹

(24) In principle, the conditions of K_2CO_3 and methanol (or THF/methanol) could have been employed, but the solubility of larger arrays in several solvents examined was insufficient for use with these solvents. Thus, for expediency we employed the unoptimized conditions described.

A mixed condensation of the BDPY-benzaldehyde **1**,¹⁸ 5-mesityldipyrromethane **2**,²⁵ and 4-iodobenzaldehyde afforded a mixture of three porphyrins (Scheme 1). The mixture was freed from non-porphyrinic impurities via silica gel chromatography. The mixture of porphyrins was separated by a second silica gel column. The BDPY-Fb porphyrin dyad **3** was obtained as the second porphyrin-containing band in 15% yield. Metalation of **3** with $\text{Zn}(\text{OAc})_2$ gave the corresponding Zn porphyrin **Zn-3**.

The Pd-mediated coupling^{26,27} of Fb porphyrin **4**³⁰ with Mg porphyrin **Mg-5**¹⁹ afforded Mg-Fb porphyrin dimer **6** in 66% yield (Scheme 2). Purification of **6** was safely effected by chromatography on grade V alumina (Mg porphyrins readily demetalate upon exposure to silica gel²¹). Treatment of **6** with TBAF gave the dimer **7** bearing a free ethynyl group.

With these two halves in hand, the linear gate was readily prepared (Scheme 2). The Pd-mediated coupling of **Zn-3** and **7** proceeded smoothly, affording a final reaction mixture consistent with that of a typical dimer-forming reaction. The chromatography on grade V alumina proceeded poorly because of streaking, which is characteristic of multiporphyrin arrays containing a Mg porphyrin.¹⁹ Nonetheless, the linear gate was obtained in 50% yield.

T Gate. The T gate molecular architecture is comprised of a short molecular wire with the switching unit appended to the Zn porphyrin transmission unit. Several synthetic routes can be envisaged to this molecular architecture. We initially prepared the T gate via a mixed Pd-mediated coupling of **11**,³¹ **14**,³² and a trans-diethynyl Mg-Zn porphyrin dimer (not shown, see Supporting Information), obtaining by extensive chromatography a few mg of the target compound for physical studies. To overcome the extensive chromatography and low yields associated with the mixed Pd-coupling approach, we have employed a stepwise synthesis of the T gate that employs an ABCD porphyrin building block (**8**, Scheme 3). The latter building block has recently become available via a new rational synthesis of ABCD porphyrins.³³ The building block **8** bears three functionalities for Pd-coupling reactions: iodo, trimethylsilylethyne, and triisopropylethyne, which are employed in this order. We chose the pattern of three functional groups to introduce the three units in

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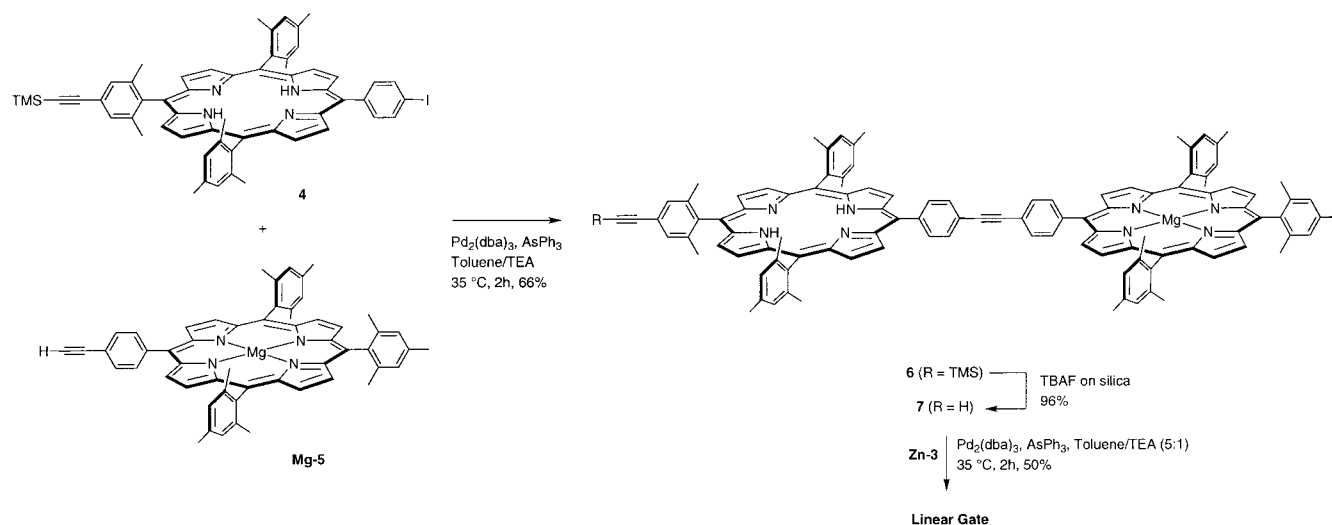
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Scheme 2



the following order: Fb porphyrin, BDPY dye, and the Mg porphyrin. There was no ideal sequence of reactions that resolved the competing constraints of the different components, given the limitations posed by extensive chromatography of multiporphyrin arrays containing Mg porphyrins, and the susceptibility of BDPY dyes to attack by the nucleophilic deprotecting agents required for removal of the TMS group or TIPS group. We chose to incorporate the BDPY dye in the penultimate step and the Mg porphyrin in the last step.

The first step in the synthesis of the T gate involved the Pd-mediated coupling of **8** and ethynyl porphyrin **5** using our recently modified Pd-mediated coupling conditions (Scheme 3).^{22,27} Isolation of dimer **9** in 53% yield was achieved by sequential chromatography (silica, SEC, silica). The TMS protecting group was selectively removed in the presence of the TIPS group by treatment of **9** with K_2CO_3 , affording dimer **10** in 87% yield. The BDPY unit was attached via Pd-mediated coupling of **11**,³¹ affording the triad **12**. Deprotection of the TIPS group in the presence of the BDPY in triad **12** was problematic, as expected. Removal of the TIPS group using TBAF on silica was found to be sluggish; upon prolonged reaction a baseline impurity appeared on silica TLC analysis, which was consistent with decomposition of the BDPY dye. Workup after the complete consumption of starting material (36 h) gave the desired triad **13** in 37% yield. Attempts to improve the yield by a shorter reaction time (4.5 h) and resubmitting the recovered starting material did not give better results, affording **13** in a total yield of 36%. Use of a solution of TBAF in THF gave **13** in 10% yield. During the course of these studies, a total of 30 mg of **13** was accumulated. This material was then used in a final Pd-mediated coupling with Mg(II)-5,10,15-trimesityl-20-(4-iodophenyl)porphyrin (**Mg-14**),²² affording the desired T gate in 36% yield following chromatographic purification (alumina, SEC, alumina). The photodynamics of gating have been thoroughly investigated for the linear and T gates.¹⁷

II. Prototypes of Refined Optoelectronic Gates

Molecular Design. (i) Redox-Switching Unit. In the linear gate and T gate a Mg porphyrin serves as

the redox-switching unit. The Mg porphyrin π -cation radical has a manifold of low-lying excited states. These excited states provide a channel for nonradiative decay of the energy initially imparted to the wire via photoexcitation. While use of the Mg porphyrin has yielded functional gates, there are several drawbacks to these complexes. (1) Mg porphyrins are somewhat labile toward demetalation; (2) streaking upon chromatography of multiporphyrin arrays containing Mg porphyrins can complicate purification; and (3) the Mg porphyrin in the neutral ground state can act as an energy-transfer acceptor with an adjacent Zn porphyrin (as in the T gate). Thus, we sought to investigate potential replacements for the Mg porphyrin for redox switching. We turned to the investigation of ferrocene as a redox-switching unit. Ferrocene exhibits reversible electrochemistry, a low oxidation potential (lower than that of the Mg porphyrin), has been widely used in electrochemical studies, and has a well-developed synthetic chemistry.

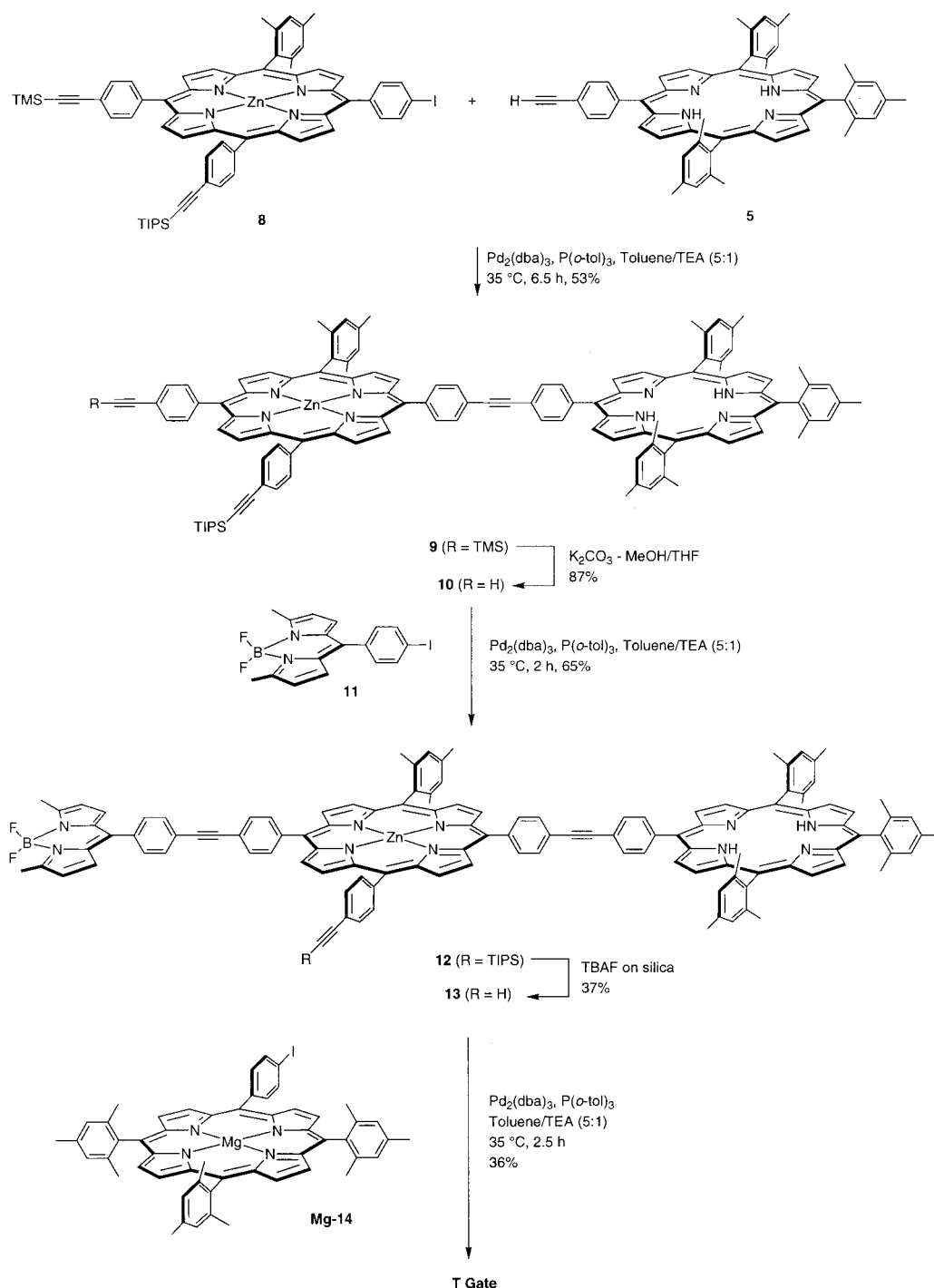
(ii) Output Unit. The linear gate and T gate were based on our original design for a molecular photonic wire. To refine this basic design, we have constructed wires that employ a phthalocyanine rather than a Fb porphyrin as the output unit.³⁴ The phthalocyanine is superior to a Fb porphyrin as an output unit for the following reasons. (1) The phthalocyanine emission is red-shifted compared with that of the porphyrin regardless of metalation state, enabling use of the Fb porphyrin as an energy-transfer component rather than only as an emitter.²⁸ (2) The fluorescence quantum yields of phthalocyanines are typically 6–10 times higher than those of porphyrins.^{35,36} (3) The emission spectra of phthalocyanines do not significantly overlap with those of porphyrins. (4) Phthalocyanines are much harder to oxidize than the corresponding porphyrins. The latter feature enables electrochemical oxidation of a wide variety of porphyrin or other (i.e., ferrocene) gating units in the presence of a phthalocyanine.

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Scheme 3



(iii) Design Targets. We sought to prepare a ferrocene–porphyrin, a ferrocene–phthalocyanine, and a ferrocene–porphyrin–phthalocyanine for fundamental studies of gating. A large number of ferrocene–porphyrins³⁷ but relatively few ferrocene–phthalocyanine dyads have been reported.³⁸ Similarly, relatively few arrays containing porphyrins and phthalocyanines have

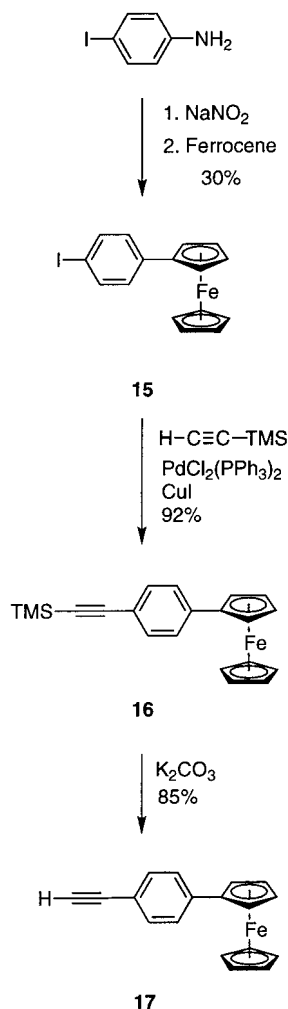
been constructed.^{28,39,40} The dearth of phthalocyanine-containing arrays reflects the difficulty of preparing phthalocyanine building blocks with specific patterns of substituents. We recently prepared a mono-ethynyl hexaheptyl substituted phthalocyanine.²⁸ This useful

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Scheme 4

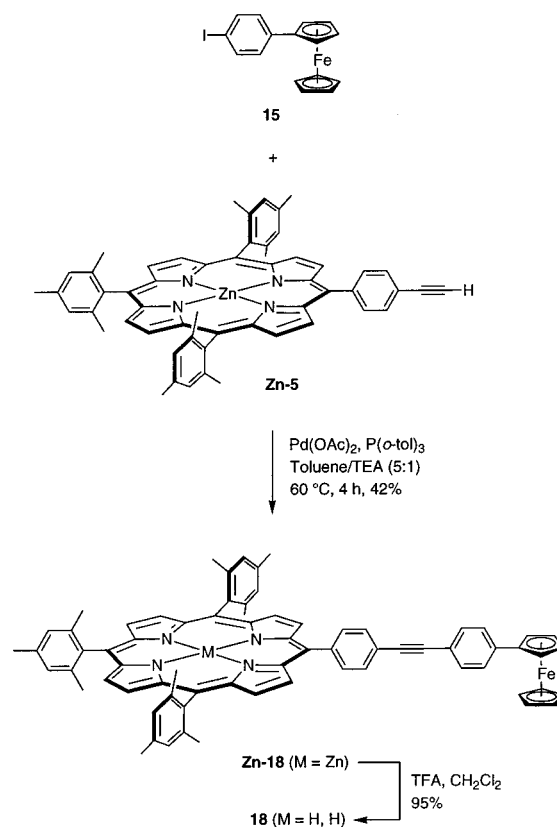


building block avoids the problem of regioisomers, which is common in phthalocyanine chemistry.⁴¹ Each porphyrin, phthalocyanine, and ferrocene building block bears a peripheral iodo or ethyne group, which provides the basis for array construction.

Synthesis. The synthesis of the ferrocene–porphyrins and ferrocene–phthalocyanines is best done through the use of appropriate ferrocene building blocks. Ferrocene readily undergoes arylation with a variety of diazonium salts.⁴² Treatment of ferrocene with a 2-fold excess of the diazonium salt of 4-iodoaniline afforded 4-iodophenylferrocene (**15**) in 30% yield (Scheme 4). The Pd-mediated coupling of **15** with trimethylsilylacetylene afforded the TMS-protected ethynylphenylferrocene (**16**) in 92% yield. Cleavage of the trimethylsilyl group in **16** using K_2CO_3 gave ethynylphenylferrocene **17** (previously synthesized using a less efficient procedure⁴³).

The Pd-mediated coupling of Zn porphyrin **Zn-5**²⁶ with (4-iodophenyl)ferrocene (**15**) afforded the ferrocene–

Scheme 5



Zn porphyrin dyad **Zn-18** in 42% yield (Scheme 5). Demetalation of **Zn-18** with trifluoroacetic acid afforded the corresponding Fb dyad **18** in 95% yield.

A phthalocyanine–ferrocene dyad **20** was synthesized in a fashion similar to that of the porphyrin–ferrocene dyad **18** (Scheme 6). The mono-ethynyl phthalocyanine building block **19** was prepared from the statistical reaction of excess 4,5-diheptylphthalonitrile and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile followed by deprotection.²⁸ The Pd-mediated coupling of phthalocyanine **19** and (4-iododophenyl)ferrocene (**15**) gave the diphenylethyne-linked ferrocene–phthalocyanine dyad **20** in 43% yield.

A triad containing a Zn porphyrin input unit, a phthalocyanine output unit, and ferrocene as the redox-switching unit was prepared to investigate the performance of the two new components in an integrated structure. For expediency we employed a mixed Pd-coupling reaction of the Zn porphyrin **21**, ethynyl ferrocene **17**, and phthalocyanine **19**. A mixture of trimeric, dimeric, and monomeric materials was obtained (Scheme 7). The purification scheme involved three chromatography procedures [silica, SEC (toluene), SEC (THF)] and afforded the desired triad **22** in 15% yield.

Electrochemistry. The solution electrochemical behavior of the ferrocene–porphyrins (**18**, **Zn-18**), ferrocene–phthalocyanine (**20**), and ferrocene–porphyrin–phthalocyanine (**22**) was investigated and is summarized in Table 1. In all cases, the potentials observed for the arrays are very similar to those observed for the individual components.^{44,45} This characteristic is indicative of the relatively weak coupling between the constituents of the arrays, as has been observed for other

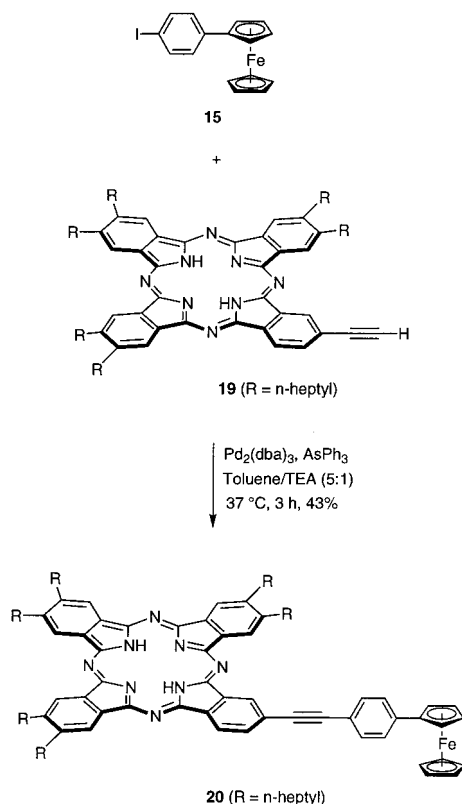
(40) (a) Li, J.; Diers, J. R.; Seth, J.; Yang, S. I.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9090–9100. (b) Li, J.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9101–9108.

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Scheme 6



multiporphyrin arrays constructed with these types of linkers.⁴⁴

Fluorescence Characterization. The fluorescence properties of the ferrocene-containing porphyrin and phthalocyanine dyads and triads were examined. Illumination of the ferrocene–Zn porphyrin **Zn-18** at 550 nm resulted in typical Zn porphyrin fluorescence but the fluorescence quantum yield was only 0.014, in comparison with 0.033 for that of ZnTPP. The Fb porphyrin analogue (**18**) also exhibited a diminished fluorescence output, with fluorescence quantum yield of 0.033 in comparison with 0.11 for that of H₂TPP. Thus, the porphyrin fluorescence emission in **Zn-18** and **18** was diminished by >50% because of the presence of the neutral (unoxidized) ferrocene. Similar quenching has been observed in other ferrocene-tethered multi-component systems.⁴⁶ The emission characteristics of the ferrocene–phthalocyanine **20** were similar to those observed for the ferrocene–porphyrins. In particular, excitation of **20** at 662 nm resulted in a typical phthalocyanine emission spectrum, but the fluorescence quantum yield was only 0.090. In contrast, the standard (*tert*-butyl)₄phthalocyanine exhibits a fluorescence quantum

yield of 0.77.³⁶ Thus, the neutral ferrocene causes quenching of 88% of the emission of the phthalocyanine output unit. However, excitation of the ferrocene–porphyrin–phthalocyanine triad **22** in the phthalocyanine absorption band (662 nm) resulted in typical phthalocyanine emission with a quantum yield of 0.79. In this case, the location of the ferrocene quite distant from the phthalocyanine resulted in little if any quenching of the fluorescence output unit.

The fluorescence characteristics of the ferrocene–porphyrins (**18**, **Zn-18**), ferrocene-phthalocyanine (**20**), and ferrocene–porphyrin–phthalocyanine (**22**) arrays were next examined under conditions where the ferrocene units were oxidized. For each of the arrays, oxidation of the ferrocene unit resulted in essentially complete quenching of the fluorescence emission from the output unit. This result indicates the ferrocene cation radical serves as an extremely efficient trap for the excited-state energy (albeit in the case of the ferrocene–Fb porphyrin and ferrocene–Zn porphyrin arrays, much of the intrinsic emission of the output units is already quenched by the neutral ferrocene unit (*vide supra*)). Accordingly, a ferrocene unit could serve as a viable redox-based switch in architectures wherein this component can be spatially removed from the energy-transfer train, as in the ferrocene–porphyrin–phthalocyanine triad **22**.

The quenching of the excited phthalocyanine output unit by the distant oxidized ferrocene redox-switching unit in **22** must occur via superexchange involving the intervening Zn porphyrin. The alternative two-step mechanism involving first energy transfer from the excited phthalocyanine to the ground-state zinc porphyrin cannot occur because this step is uphill by about 0.17 eV ($\approx 6.6 k_B T$). Superexchange-mediated quenching of a distant excited output unit such as a phthalocyanine by the ferrocene redox-switching unit is analogous to the operation of the T gate (and related triads containing Mg, Zn, and Fb porphyrins). In these architectures, an oxidized Mg porphyrin effectively shunts the distant photoexcited free base porphyrin output unit using the intervening zinc porphyrin as a superexchange mediator.¹⁷ However, the finding that ferrocene can serve the same redox-switching function as porphyrins if distant from the output unit offers additional flexibility in design, whereby differences in redox, optical absorption, and other properties of the redox-switching units can be taken into account.

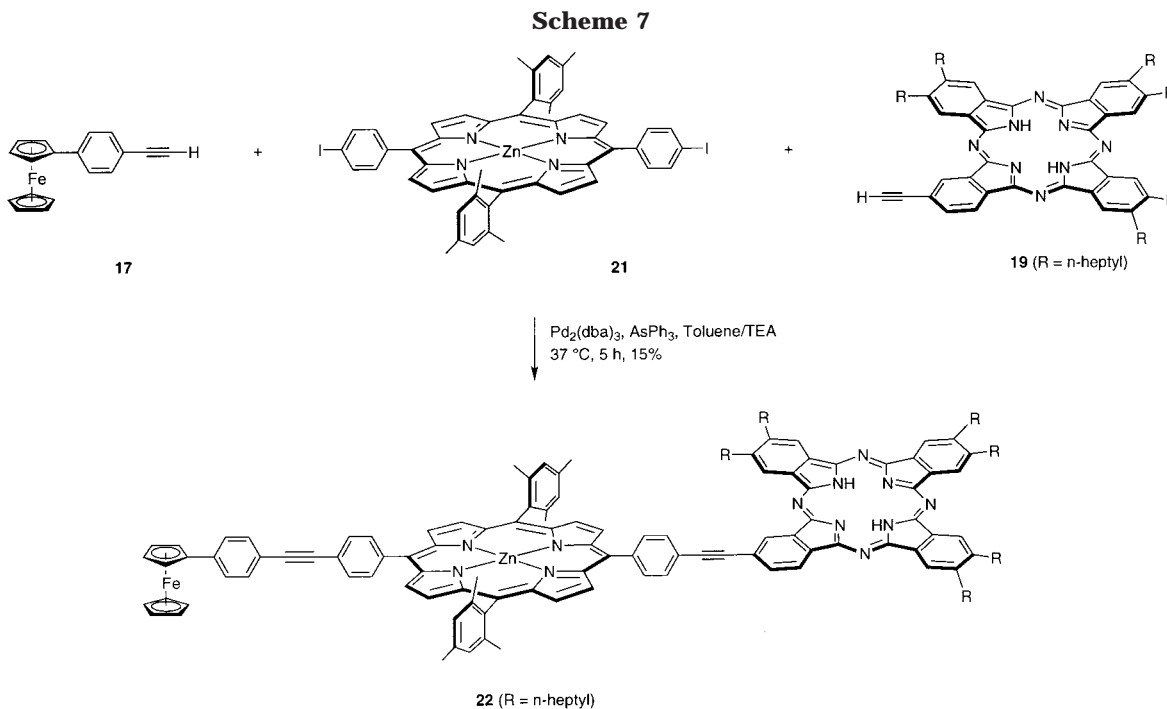
III. Toward an All-Optical Gate

Molecular Design. The gating process in the linear gate and T gate involves the introduction of an oxidized species in close proximity to the components of the molecular wire. In all of the gates prepared previously, oxidation is achieved chemically or electrochemically. In an effort to develop an all-optical gate, we sought to generate an oxidized species in a transient manner via the use of light rather than by chemical or electrochemical means. Inorganic coordination compounds in which a strong metal-to-ligand charge-transfer (MLCT) transition occurs upon photoexcitation are excellent candidates as components in an optical gate. For example, in Ru(bpy)₃X₂, photoexcitation results in charge transfer from the Ru²⁺ ion to the bpy ligands, effectively creating

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(45) The reported electrochemical potentials for phthalocyanine monomers often reflect aggregation, making direct comparisons with porphyrins and ferrocene difficult. (See: Lever, A. B. P.; Milaeva, E. R.; Speier, G. In *Phthalocyanines, Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1993; Vol. 1, pp 1–69.) Nevertheless, the oxidation potential of a phthalocyanine is expected to be higher than that of a corresponding porphyrin, consistent with the trends in measured redox properties of the arrays.

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**Table 1. Half-Wave Potentials of the Arrays^a**

| array | ferrocene | | porphyrin | | phthalocyanine | | Ru(L) ₂ L' ^c | | |
|--------------|--------------------|------------------|---------------------------------|--------------------|------------------------------------|------------------|------------------------------------|-------|--|
| | Fc/Fc ⁺ | P/P ⁺ | P ⁺ /P ²⁺ | Pc/Pc ⁺ | Ru ²⁺ /Ru ³⁺ | L/L ⁻ | L'/L ⁻ | | |
| 18 | 0.23 | 0.68 | <i>b</i> | | 1.16 | | | | |
| Zn-18 | 0.23 | 0.59 | 0.88 | | | | | | |
| 20 | 0.24 | | | | 1.16 | | | | |
| 22 | 0.19 | 0.56 | 0.90 | | 1.17 | | | | |
| 30 | | 0.56 | 0.90 | | | 1.19 | -1.12 | -1.31 | |

^a Obtained in CH₂Cl₂ (except for **30**, BuCN) containing 0.1 M TBAH using techniques and instrumentation previously described.⁴⁴ Potentials vs Ag₂/Ag⁺; E_{1/2}(Fc/Fc⁺) = 0.20; scan rate 0.1 V/s, values are ±0.01 V. ^b Wave not observed, but probably overlaps with wave for the phthalocyanine. ^c The L and L' refer to the 2,2'-bipyridyl and diester-substituted 2,2'-bipyridyl ligands, respectively.

a Ru³⁺-(bpy)⁻ charge-separated state.⁴⁷ The Ru³⁺ state is an extremely strong oxidant that could potentially promote facile oxidation of an adjacent porphyrin (via charge transfer to the Ru³⁺ ion).⁴⁸ This process obviously requires that the rate of electron transfer from the porphyrin to the Ru³⁺ ion is significantly faster than the rate of charge recombination of the Ru³⁺-(bpy)⁻ charge-separated state in the complex. To investigate this possibility and to determine whether this basic molecular design could function as an optically driven redox switch, we sought to develop a scheme whereby a Ru(bpy)₃X₂ derivative is placed adjacent to a porphyrin. To spatially remove the electron initially photo-transferred from Ru²⁺ to the bpy ligands from proximity with the porphyrin, we elected to use a derivative of Ru(bpy)₃X₂ in which the two nonlinking ligands are substituted with electron-withdrawing substituents. A variety of such heteroleptic ruthenium coordination compounds have been prepared.^{48,49} The appropriate choice of substituents also leads to a red-shift of the main absorption band of the Ru(bpy)₃X₂ derivative into the window between the B- and Q-bands of the porphyrin.

Synthesis. We sought to prepare a dyad comprised of a Ru(bpy)₃X₂ derivative attached to a porphyrin for studies of optical gating phenomena. Although such a dyad alone would not comprise an all-optical gate, a dyadic motif exhibiting suitable photochemical behavior could be incorporated as an optical-switching unit in a larger all-optical gate architecture. A sizable number of dyads (or larger architectures) comprised of a porphyrin and a Ru(bpy)₃ complex,⁴⁹ Ru(tpy)₃ complex,⁵⁰ or other metal complex⁵¹ have been synthesized. The photochemical properties of a number of such complexes (with identical ligands at the metal center) have been reviewed.⁵² The prior synthetic work suggested two possible routes for the preparation of the Ru(bpy)₃X₂-

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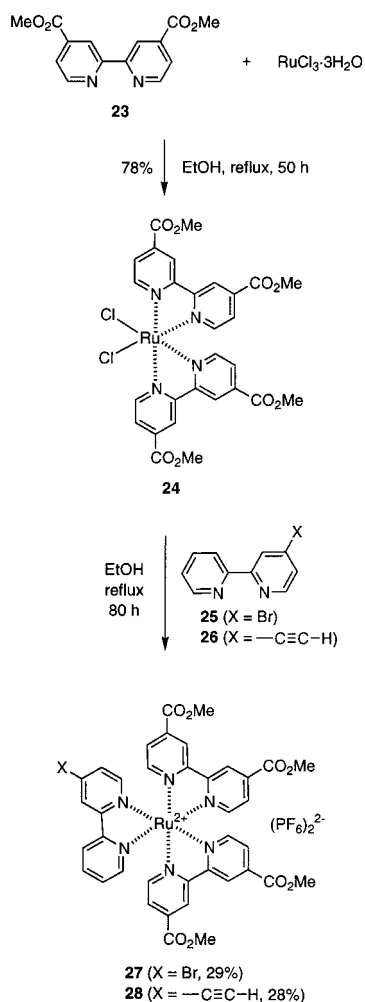
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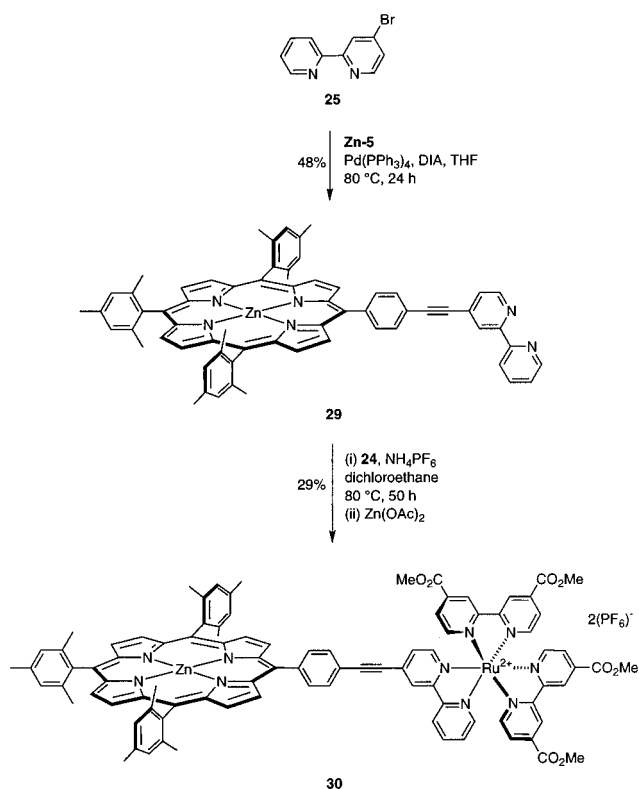
Scheme 8



Zn porphyrin dyad: (1) The dyad could be constructed by the Pd-mediated coupling of a porphyrin with an iodo- or ethynyl-substituted heteroleptic Ru-based complex; (2) a porphyrin–bipyridyl moiety could be prepared first and then reacted with a suitable $(\text{bpy}')_2\text{RuCl}_2$ complex. While both routes have merits, the former route was pursued first.

The requisite dimethyl bipyridyl-4,4'-dicarboxylate (**23**)⁵³ and 4-bromobipyridyl (**25**)⁵⁴ were prepared from 4,4'-dimethylbipyridyl and bipyridyl, respectively, following literature procedures. Refluxing a 1:2 mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and dimethyl bipyridyl-4,4'-dicarboxylate (**23**) in 95% ethyl alcohol for 50 h under argon afforded the complex **24** in 78% yield (Scheme 8). Reaction of the latter with 4-bromobipyridyl (**25**) gave the desired heteroleptic ruthenium complex **27** in 29% yield. However, the final Pd-catalyzed coupling reaction of **27** with a zinc mono-ethynyl porphyrin (**Zn-5**) did not yield the desired **30** because of decomposition of the ruthenium complex.

Scheme 9



Next, we interchanged the functionalities required for the Pd-coupling reaction. Accordingly, the reaction of the bipyridyl complex **24** with ethynyl bipyridyl **26**⁵⁵ (in a manner similar to that employed for the synthesis of **27**) afforded the ruthenium complex **28**. However, the Pd-mediated coupling of the ruthenium complex **28** with zinc(II)-5-(4-iodophenyl)-10,15,20-trimesitylporphyrin (**Zn-14**)²² also failed to give the target molecule **30**.

Subsequently, the second synthetic route was investigated. The Pd-mediated coupling of 4-bromobipyridyl (**25**) and the Zn porphyrin **Zn-5** afforded the corresponding Zn porphyrin bearing a bipyridyl moiety (**29**) in 48% yield (Scheme 9). A mixture of porphyrin **29**, ruthenium complex **24**, and NH_4PF_6 in anhydrous dichloroethane was heated for 50 h under argon in the dark, affording the crude dyad containing the Fb porphyrin (due to demetalation). Treatment of the latter with methanolic zinc acetate gave the desired optical gate **30** in 29% yield.

Electrochemistry. The redox properties of ruthenium complex **24** were investigated and are summarized in Table 1. The value of the $\text{Ru}^{2+}/\text{Ru}^{3+}$ couple for the complex is ≈ 1.19 V. This value is consistent with that expected for a $\text{Ru}(\text{bpy}')_3\text{X}_2$ complex with similar ligands.⁴⁸ The potential of the $\text{Ru}^{2+}/\text{Ru}^{3+}$ couple is well positive of that of the Zn porphyrin constituent (≈ 0.56 V). Thus, considering only the redox properties, the complex has the requisite characteristics to facilitate generation of a porphyrin π -cation radical upon photoexcitation of the ruthenium complex. This would both quench the fluorescence of the porphyrin and allow the oxidized porphyrin to quench nearby excited states in larger architectures.

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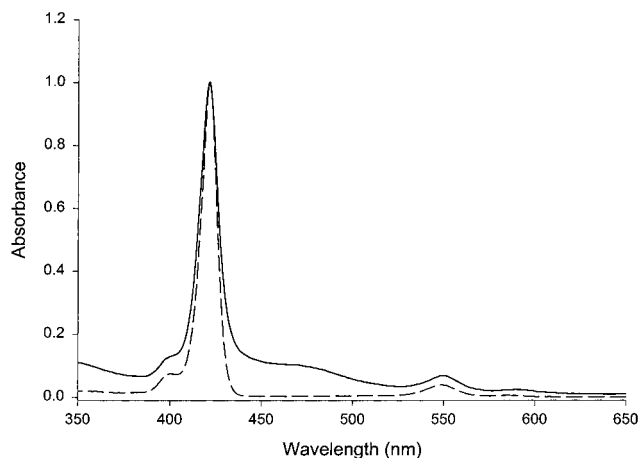


Figure 2. Absorption spectra of **30** (solid line) and Zn(II)-5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,15,20-trimesitylporphyrin²⁰ (dashed line) in CH₂Cl₂ at room temperature. The absorption spectra are normalized at the B-band.

Absorption and Fluorescence Characterization.

The absorption spectrum of the Zn porphyrin–ruthenium complex **30** in dichloromethane is shown in Figure 2. The absorption spectrum of a monoethynyl Zn porphyrin is also shown for comparison purposes. The spectrum of **30** shows the typical porphyrin B and Q absorption bands at 421 and 551 nm, respectively. In addition, a broad featureless absorption is observed in the window between the B- and Q-bands. The latter absorption is due to the ruthenium complex. The magnitude of the absorption at 470 nm ($\epsilon = 63\,000\text{ M}^{-1}\text{ cm}^{-1}$), although much weaker than that of the porphyrin B band, is sufficient for relatively selective excitation of the ruthenium complex in the presence of the porphyrin.

The fluorescence behavior of ruthenium complex **30** was investigated. The emission from the Zn porphyrin component ($\Phi_f = 0.0012$) was reduced by 28-fold from that of zinc tetraphenylporphyrin ($\Phi_f = 0.033$). The apparent quenching of the excited zinc porphyrin by the Ru(bpy)₃X₂ complex prompted us to carry out transient absorption studies in which the Zn porphyrin unit in **30** was excited with a 120-fs flash at 550 nm. This results in complete deactivation to the ground state in tens of picoseconds, in full accord with the fluorescence quenching behavior. In fact, the time-resolved optical data show that the quenching process involves two very fast steps. These steps most likely involve charge transfer from the photoexcited Zn porphyrin to the ground-state Ru(bpy)₃X₂ complex in <1 ps followed by rapid charge recombination, giving the ground state in ≈ 10 ps. Such charge-transfer processes indicate the Ru(bpy)₃X₂–Zn porphyrin complex is well suited for use as an optical-switching unit in a larger molecular device. However, the extremely fast and efficient quenching of the photoexcited porphyrin by the adjacent ground-state Ru(bpy)₃X₂ complex precludes direct attachment of the Ru(bpy)₃X₂ complex to a Zn porphyrin component of the energy-transfer train in an all-optical gate. On the other hand, placement of the ruthenium complex at a site more distant from the energy-transfer train (as done with the ferrocene in **22**) should substantially mitigate the problem of excited-state quenching. For example, the Ru(bpy)₃X₂ unit could be attached to a Zn porphyrin

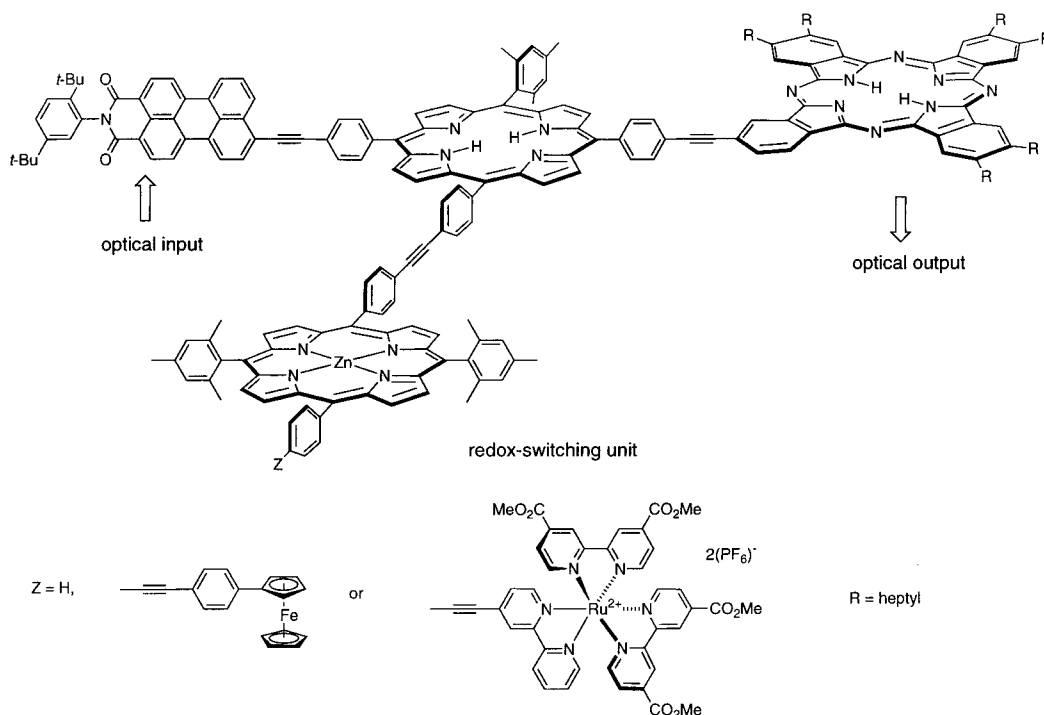
(or Mg porphyrin) unit, which is in turn attached to a Fb porphyrin output unit in the linear gate design.

IV. Outlook

The results obtained from preparation and examination of these gates can be used to design refined molecular optoelectronic gates. A T-gate architecture remains quite attractive, whereby quenching of the excited state is achieved by a redox-switching unit located on the wire component of the device (rather than on the output unit as in the linear gate). A key design objective is to employ a redox-switching unit that cannot accept excited-state energy from the energy-transfer train in the molecular wire unit of the device. Refined T gates that meet this objective are shown in Chart 3. These designs also incorporate features from a molecular wire that we recently synthesized, which is composed of a perylene–monoimide dye, two intervening porphyrins, and a phthalocyanine.³⁴

The energy-transfer train in the refined T gates is comprised of a perylene mono-imide (input unit), a Fb porphyrin (transmission unit), and a Fb phthalocyanine (output unit). The redox-switching unit is comprised of either a Zn porphyrin, a ferrocene–Zn porphyrin, or a Ru(bpy)₃X₂–Zn porphyrin. The advantages of each of these components are as follows: (1) A perylene-monoimide dye of the type shown in Chart 3 exhibits a monophasic excited-state lifetime and nearly unity fluorescence quantum yield. In contrast, the BDPY dye exhibits a biphasic lifetime and rather low fluorescence yield.¹⁸ The existence of the dual lifetime, which stems from two excited-state conformers, renders interpretation of kinetic data concerning energy-transfer dynamics in BDPY–porphyrin arrays rather difficult. A perylene-monoimide–porphyrin dyad exhibits fast and efficient energy transfer from perylene to porphyrin.³⁴ (2) The Fb phthalocyanine exhibits a very high fluorescence quantum yield (≈ 0.7 – 0.8) and is exceptionally resistant to oxidation. In addition, the red-shifted absorption and emission spectra of the phthalocyanine compared with that of the porphyrin (Zn or Fb) enable use of a Fb porphyrin as an energy-transfer donor. (3) Fb porphyrins are excellent energy-transfer donors and are exceptionally resistant to oxidation in the ground and excited states. We have prepared porphyrin–phthalocyanine dyads and found that the all-free base system affords rapid energy transfer from porphyrin to phthalocyanine.²⁸ In addition, the use of a Fb porphyrin as the transmission unit enables the use of a Zn porphyrin as one (or the sole) component in the redox-switching unit. The Zn porphyrin is more easily oxidized than a Fb porphyrin. (4) The main advantages of the Zn porphyrin compared with a Mg porphyrin in the redox-switching unit are as follows. First, the Zn porphyrin is less labile toward demetalation. Second, energy transfer does not occur from the Fb porphyrin to the Zn porphyrin (in contrast with rapid energy transfer from the Zn porphyrin to the Mg porphyrin in the original T gate). The redox-switching unit can consist of the Zn porphyrin alone, a ferrocene–Zn porphyrin (as in **22**), or a Ru(bpy)₃X₂–Zn porphyrin. The ferrocene enables oxidation at lower potential than that of the Zn porphyrin, whereas the Ru(bpy)₃X₂–Zn porphyrin should

Chart 3



enable the Zn porphyrin cation radical to be formed photochemically. The ferrocene and $\text{Ru}(\text{bpy})_3\text{X}_2$ components can be used effectively without causing quenching (in the neutral/ground state) of excited-state energy migration along the energy-transfer train in the molecular wire unit of the device. This is true because these redox-switching components are located at sites distant from the energy-transfer train and are attached to a Zn porphyrin which cannot accept energy from the Fb porphyrin component of the energy-transfer train. These design considerations should lead to optoelectronic gates with enhanced performance and stability.

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Supporting Information Available: Complete Experimental Section describing the synthesis of all new compounds (**3**, **Zn-3**, **7**, **8-10**, **12**, **13**, **15-18**, **Zn-18**, **20-22**, **24**, **27-30**, linear gate, T gate); ^1H NMR spectra for all new compounds; LD-MS spectra for all new porphyrins and porphyrin arrays; and a description of the approach used for the initial synthesis of the T gate (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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