A potential and ion switched molecular photonic logic gate†

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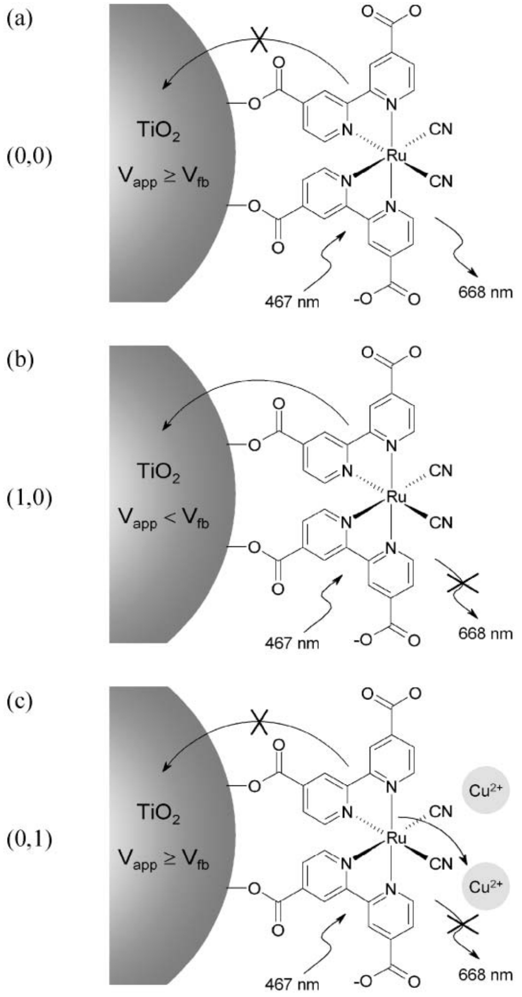
A molecular photonic logic gate is demonstrated by integrating electrical (potential) and chemical (ionic) switching functions into molecules attached at an externally addressable semiconductor substrate.

Recent advances in supramolecular chemistry and nanomaterials research have stimulated interest in the design and development of molecular electronic and photonic devices for information processing, sensing and computation.[1] Numerous examples of molecular nanodevices operating as wires,[2] switches[3] and sensors[4] have been reported in the literature. The development of molecular scale logic gates responding to multiple inputs has been a particularly active area of research.[5] Specifically, photoluminescent logic gates exhibiting AND,[6] OR,[7] XOR,[8] NOR[9] and INH[10] functionality have all been demonstrated. Exploitation of molecular photonic properties is appealing in this regard due to the high absorption cross-sections and luminescence efficiencies of many molecular systems, as well as the high signal-to-noise ratios that may be achieved.

However, the majority of these supramolecular systems operate exclusively in the solution phase, thus limiting the range of inputs that may be used to ions and other chemical species, or simple environmental stimuli such as temperature.[11] The lack of an externally addressable interface makes it uncertain whether these approaches can provide a viable and scalable technology suitable for integration into future hybrid nanoelectronic devices and circuits. To successfully address this challenge, it will be necessary to take advantage of the structural and electronic properties of molecules for the rational design and fabrication of photonic logic gates that can be addressed by an underlying metal or semiconductor substrate. To this end, we report on the demonstration of an externally addressable molecular photonic logic gate comprising a metal polypyridyl complex self-assembled at the surface of a nanocrystalline semiconductor electrode that responds to electrical and chemical inputs provided by the substrate and the ambient solution, respectively.



Scheme 1 Design and operating principles of the integrated molecular photonic logic gate. (a) Under negative applied potentials and in the absence of Cu^{2+} ions (0,0), visible excitation of the Ru^{II} complex results in a strong MLCT based luminescence output. The luminescence output may be switched off by either (b) the application of positive applied potentials in the absence of Cu^{2+} ions (1,0), (c) the introduction of Cu^{2+} ions into the adjacent electrolyte solution under negative applied potentials (0,1) or (not shown) the introduction Cu^{2+} ions into the adjacent electrolyte solution under positive applied potentials (1,1)

Scheme 1 outlines the design and operating principles of the system selected for study, *cis*-bis(cyano) ruthenium(II)-bis-2,2′-bipyridine-4,4′-dicarboxylate ($Ru(dcbpy)_2(CN)_2$, **I**), adsorbed at the surface of a nanoporous nanocrystalline TiO_2 thin film. Chelation of **I** onto the TiO_2 substrate *via* its pendant carboxylate groups[12] allows for both electrical and chemical switching functions to be integrated into a single molecular device. The

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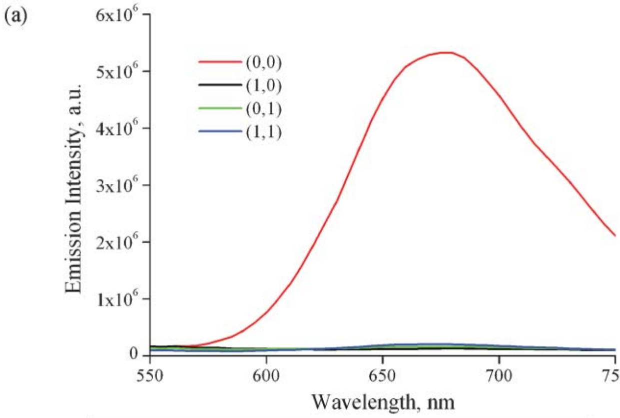
electrical switching function is accomplished by modulating the potential applied to the semiconductor substrate, employed as the working electrode in a three-electrode single compartment electrochemical cell. It is well known that dye sensitization of TiO_2 films usually results in quenching of dye luminescence as a consequence of efficient excited state mediated electron transfer to the TiO_2 conduction band.[13] However, luminescent emission from the dye may also be switched on at applied potentials more negative than the TiO_2 flat band potential (V_{fb}) due to the sharp reduction in charge injection yields that occurs following increased occupancy of the electronic density of states with the electrode.[14–16]

Therefore, at applied potentials more negative than the TiO_2 V_{fb} (0,0), visible excitation of the Ru^{II} complex results in a strong metal-to-ligand charge transfer (MLCT) based luminescence in the red; see Scheme 1(a). In contrast, application of a more positive bias, (1,0), leads to almost complete luminescence quenching due to charge injection from the ^{1}MLCT and thermalised ^{3}MLCT excited states of the Ru^{II} complex into the TiO_2 conduction band;[14–16] see Scheme 1(b). The second switching function is accomplished by introduction of Cu^{2+} ions into the adjacent electrolyte solution; see Scheme 1(c). Luminescence quenching by Cu^{2+} ions has been previously reported in solution phase studies of the $Ru(bpy)_2(CN)_2$ complex.[17] Here, formation of $[Ru(bpy)_2(CN)(CNCu)]^{2+}$ and $[Ru(bpy)_2(CNCu)_2]^{4+}$ species results in static quenching of complex luminescence. Dynamic quenching, *i.e.*, luminescence quenching by unbound metal cations diffusing from solution, is also a significant additional pathway.[17]

These switching functions were combined to demonstrate a two-input molecular photonic logic gate, using the MLCT based luminescence of the complex as the output signal, and the potential applied to the semiconductor substrate, in the presence or absence of Cu^{2+} ions, as the input signals. Complex **I** was synthesized according to previously reported procedures; see Supporting Information.† **I** was adsorbed from solution onto the surface of a nanostructured TiO_2 (anatase) thin film on fluorine-doped tin oxide coated glass. The **I**-functionalized substrate was incorporated as the working electrode in a single compartment spectroelectrochemical cell, with a Pt rod counter electrode and an Ag/AgCl reference electrode. Fig. 1(a) shows the emission spectra of a **I**-functionalized nanocrystalline TiO_2 film recorded under each of the four possible input conditions. In the (0,0) state, excitation at 467 nm results in strong complex phosphorescence with a maximum at 668 nm. In the (1,0) state, this emission is switched off by the applied positive bias due to luminescence quenching by charge injection. In the (0,1) state, *i.e.*, at negative applied potentials, but in the presence of added Cu^{2+} ions, the emission is also switched off. Finally, in the (1,1) state, both switching functions can contribute to quenching of the MLCT based luminescence, thus completing the NOR logic gate truth table; see Fig. 1(b). Comparison of the output luminescence intensity of the (0,0) state with that of each of the three other states gives an average device on/off ratio of *ca.* 30 : 1 (at 668 nm), a value that compares very favourably with those obtained for solution based molecular logic gates.[6–11]



(b)

Input 1 (V_{app})	Input 2 ([Cu^{2+}])	Output (MLCT Emission)
0	0	1
1	0	0
0	1	0
1	1	0

Fig. 1 (a) Emission spectra of a **I**-functionalized nanocrystalline TiO_2 film recorded as a function of applied potential and the presence of Cu^{2+} ions. Electrolyte solution: 0.1 M $LiClO_4$ in CH_3CN. (b) Corresponding NOR gate truth table, where V_{app} = 0 indicates $V_{app} \geqslant V_{fb}$, V_{app} = 1 indicates $V_{app} < V_{fb}$, and [Cu^{2+}] = 1 indicates the presence of added Cu^{2+}.

In summary, we have shown for the first time that a molecular photonic logic gate may be constructed by integrating electrical and chemical switching functions into molecules adsorbed at an externally addressable semiconductor substrate. These results suggest that this approach may provide a scalable strategy for the fabrication of future molecular level optoelectronic devices.

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