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Modification of Fluorescent Photoinduced Electron Transfer (PET) Sensors/Switches To Produce Molecular Photo-Ionic Triode Action**

Allen J. M. Huxley, Marc Schroeder, H. Q. Nimal Gunaratne, and A. Prasanna de Silva*

Dedicated to Prof. Seiji Shinkai

Abstract: The fluorophore-spacer₁-receptor₁-spacer₂-receptor₂ system (where receptor₂ alone is photoredox-inactive) shows ionically tunable proton-induced fluorescence off-on switching, which is reminiscent of thermionic triode behavior. This also represents a new extension to modular switch systems based on photoinduced electron transfer (PET) towards the emulation of analogue electronic devices.

Fluorescent photoinduced electron transfer (PET) sensors/systems[1–4] are a well-established application of molecular systems, to the point of real-life deployment worldwide in blood electrolyte diagnostics.[5–8] Important picosecond laser studies on fluorescent PET sensors/switches have demonstrated the transient existence of radical ion species[9–11] and thus designers can proceed with confidence. As a result of their modular fluorophore-spacer-receptor construction, fluorescent PET systems are very amenable to modification in terms of the format, as well as in terms of the detailed functionalities. The latter approach has yielded many individual examples of sensors and switches based on fluorescence which target important analytes.[12–15] On the other hand, the former approach has the potential to set up new areas of endeavor and application, which is exploited here.

The controllable quenching of molecular fluorescence[12,13] can be exploited to build switchable systems which emulate familiar electronic devices. Some of these molecular systems have unique applications which are inconvenient for their electronic counterparts, such as wireless operation in microfluidic spaces.[16] The first molecular logic gate[17–23] (an advanced molecular switch)[24] was a fluorophore-spacer₁-receptor₁-spacer₂-receptor₂ system, where two photoinduced electron transfer (PET)[1,27] channels arising from the two receptors were controlled by binding H⁺ and Na⁺ ions, respectively, and thus the fluorescence output corresponded to photo-ionic AND logic. Strong fluorescence emerges only when all PET processes are suppressed (Figure 1a).[4] Related, but distinct, fluorophore-spacer₁-receptor₁-spacer₂-receptor₂ systems,[28] where both receptors respond to H⁺ ions, for example, 2, give rise to fluorescent off-on-off action, which can correspond to ternary logic behavior.[22] We now demonstrate aspects of molecular photo-ionic triode action for the first time by structurally mutating the fluorophore-spacer₁-receptor₁-spacer₂-receptor₂ system 1 into a novel format exemplified by 3, where the convenient photoredox capability of receptor₁ is removed from 1 (Figure 1b). Nearly 20 distinct formats of luminescent PET switching systems, each possessing its own defining features and applications, are known.[29] Fluorescence off-on switching is, therefore, controlled within 3 by selective ion binding of receptor₁. This switching profile is influenced by the orthogonally selective ion binding of receptor₁, which is forced into a secondary role (Figure 1b). The amine receptor, within 3 would bind H⁺ instead of alkali and alkaline earth cations. The crown ether receptor, within 3 would bind alkali and alkaline earth cations instead of H⁺. This photo-ionic triode action complements molecular all-photonic triode behavior, which was reported recently by Gust, Moore, and co-workers.[29] Molecular all-electronic transistor action, and logic gates arising therefrom, is also known.[30,31] It is also important to note a different conceptual approach to a molecular triode based on PET, as described by Verhoeven and co-workers.[12]

The electronic triode[32] (the forerunner of the transistor)[33] is a fundamental switch and consists of a vacuum tube containing a hot filament undergoing thermionic emission of electrons which are collected by a plate electrode, provided the latter is at a sufficiently positive voltage. The plate current (i_P) output is essentially a sigmoidal function of the plate voltage (V_P) input because the electron current saturates at highly positive voltages, owing to the limited supply of electrons from the filament. The triode contains a grid electrode between the filament and the plate. The voltage of the latter (V_G) sensitively controls electron traffic, that is, the i_P-V_P characteristic curve is shifted along the voltage axis depending on the value of V_G (Figure 1c). Compound 3 shows a very similar effect at the molecular level when its fluorescence emission spectrum is examined under various ionic conditions (Figure 2a). The fluorescence quantum yield (φ_F) output is a sigmoidal function of the pH input and the shift of the φ_F-pH curve along the pH axis depends on the presence of another cation which lodges in the [15]crown-5
for the fluorescence data. The $pK_a$ values determined by fluorescence spectroscopy agree with the corresponding values obtained by absorption spectroscopy, even though the latter values are only estimates because of the small absorption changes that are seen (Table 1).

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$\log((\phi_{\text{trans}} - \phi)/(\phi - \phi_{\text{trans}})) = \text{pH} - pK_a$

Figure 1. a) A fluorophore for photon transactions and two receptors for ion binding are the three crucial components of the molecular AND logic gate, where the two spacers serve as connectors. b) In a similar vein, the three crucial components of the molecular photoionic triode consist of a fluorophore and a principal receptor, alongside an auxiliary receptor. The latter endows the system with a way of tuning the input/output (I/O) characteristic curve. c) The three crucial components of the vacuum thermionic triode consist of a filament, plate, and an interspersed grid. This set-up also produces a tunable input/output (I/O) characteristic.

Figure 2. a) Fluorescence emission spectra for $10^{-3} \, \text{M} \, 3$ in methanol/water (1:1, v/v) with $10^{-5} \, \text{M}$ morpholinopropylsulfonic acid in the presence of $0.3 \, \text{mM} \, \text{Me}_4\text{NCl}$, when excited at 369 nm. pH adjustments were performed with $\text{Me}_4\text{NOH}$ and $\text{HCl}$. The pH values in order of decreasing fluorescence intensity are: 6.4, 7.6, 8.2, 8.5, 8.7, 8.9, 9.5, 9.8, and 10.3. It is notable that all the spectral features except the quantum yield are essentially independent of the pH value, as expected for fluorescent PET sensors containing luminophores with $\pi\pi^*$ excited states. Similar spectra are found when $\text{Me}_4\text{NCl}$ is replaced by other salts (see below). b) Fluorescence quantum yield ($\phi$)-pH profiles for 3 in the presence of various chloride salts. The concentrations of monovalent cation salts and divalent cation salts were chosen to minimize ionic strength changes. The salt concentrations were chosen to allow for as much as possible of 3 to be bound to the cation through the crown ether, while respecting solubility limits. Such a choice is enabled by data tables of cation/crown ether binding constants. Studies at lower salt concentrations were not conducted since those would require dissection of the $\phi$-pH profiles into metal-free and metal-bound components, with large attendant uncertainties. The cations employed were: $0.3 \, \text{mM} \, \text{Me}_4\text{N}^+$ (filled squares), $0.3 \, \text{mM} \, \text{Na}^+$ (open diamonds), $0.3 \, \text{mM} \, \text{K}^+$ (filled triangles), $0.3 \, \text{mM} \, \text{Ca}^{2+}$ (filled diamonds), $0.1 \, \text{mM} \, \text{Sr}^{2+}$ (open circles), and $0.1 \, \text{mM} \, \text{Ba}^{2+}$ (open triangles). The full lines are calculated according to Equation (1), by employing the experimentally determined parameters $pK_a$, $\phi_{\text{trans}}$, and $\phi_{\text{trans}}$ from Table 1.
Acidity constants and fluorescence quantum yield data for Table 1:

<table>
<thead>
<tr>
<th>Cation</th>
<th>pK_a</th>
<th>pK_a[H]</th>
<th>Φ_max</th>
<th>Φ_min</th>
<th>Φ_max</th>
<th>Φ_min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄N⁺</td>
<td>8.6</td>
<td>8.3</td>
<td>0.37</td>
<td>0.040</td>
<td>8.2</td>
<td>0.37</td>
</tr>
<tr>
<td>Na⁺</td>
<td>8.0</td>
<td>8.0</td>
<td>0.36</td>
<td>0.040</td>
<td>8.2</td>
<td>0.38</td>
</tr>
<tr>
<td>K⁺</td>
<td>8.3</td>
<td>8.3</td>
<td>0.38</td>
<td>0.036</td>
<td>8.3</td>
<td>0.36</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>8.3</td>
<td>8.3</td>
<td>0.38</td>
<td>0.032</td>
<td>8.0</td>
<td>0.37</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>8.0</td>
<td>[H]</td>
<td>0.38</td>
<td>0.048</td>
<td>8.0</td>
<td>0.36</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>7.6</td>
<td>[H]</td>
<td>0.40</td>
<td>0.048</td>
<td>8.3</td>
<td>0.38</td>
</tr>
</tbody>
</table>

[a] Conditions as given in Figure 2. The fluorescence-based pK_a values, which were determined according to Equation (1), have uncertainties of ±0.1. The Φ values have uncertainties of ±10% and were determined by comparison with secondary standards in Ref. [35]. [b] Data estimated by analysis of small H⁺-induced changes in the UV absorption spectra according to the corresponding version of Equation (1). [c] Spectral changes are too small to permit an estimate to be made.

To conclude, the tunable I/O characteristic of a molecular photo-ionic device which emulates thermionic triode behavior, that is, signal amplification, is well-known in other chemical systems.

We have here a rarely noted supramolecular substituent effect[37] on pK_a values, where the cation serves as the substituent. Physical organic chemistry usually deals with the effects of substituents which are covalently attached to the structure carrying the reactive site.[38] Although many cases of ion-induced pK_a shifts are available,[39–43] the concept of photo-ionic triode action is unprecedented. An elegantly tunable PET sensor for glucose developed by James and Shinkai[44] does not correspond to photo-ionic system by the use of three active units within the electrode philosophy of the triode is also followed in the new format of fluorescent PET switches. The three-ion triode action is unprecedented. An elegantly tunable PET sensor for glucose developed by James and Shinkai[44] does not correspond to photo-ionic system by the use of three active units within the electrode philosophy of the triode is also followed in the new format of fluorescent PET switches. The three-ion triode action is unprecedented.


