Advances in Supramolecular Chemistry

ADVANCES IN SUPRAMOLECULAR CHEMISTRY

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PREFACE

The goal in Volume 4 of *Advances in Supramolecular Chemistry* remains the same as for previous volumes: to present a broad range of supramolecular science recorded by an international panel of distinguished researchers. Contributions in this volume span the scientific range from electronic device development to novel synthetic receptor molecules to biomimetic ion channels.

The true breadth of the supramolecular chemistry field is sometimes overlooked. By their very nature, focused monographs cannot span the range of efforts that include analytical, inorganic, organic, physical, and biochemistry. Even considering the wide range of studies underway, there is some polarization between the biological side of supramolecular science and materials development. It is hoped that the quality of the presentations in this volume will demonstrate that there is original, fascinating, and excellent science on both sides and throughout the field of supramolecular chemistry.

George W. Gokel
Editor

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SUPRAMOLECULAR PHOTOIONIC DEVICES:

PHOTOINDUCED ELECTRON TRANSFER (PET) SYSTEMS WITH SWITCHABLE LUMINESCENCE OUTPUT

A. Prasanna de Silva, H. Q. Nimal Gunaratne, Thorfinnur Gunnlaugsson, Allen J. M. Huxley, Colin P. McCoy, Jude T. Rademacher, and Terence E. Rice

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1. INTRODUCTION

In this review we aim to demonstrate that supramolecular devices which operate via the interconversion of ionic and photonic signals can be useful for the gathering and processing of chemically relevant information. We will restrict ourselves to discussing those systems which involve the competing processes of luminescence emission and PET (photoinduced electron transfer). The emphasis will be placed on the recent literature.

2. WHY PHOTOIONIC DEVICES?

The usefulness of supramolecular systems[1–4] which operate with ionic inputs and luminescence output stems from many features.

Ions were present at the creation of supramolecular chemistry. It is remarkable that all three inventors of the field commenced their research by designing and constructing receptors for ions of the s-block in the periodic table.[5–7] Therefore researchers into photoionic devices have the rare benefit of drawing on the entire resources of a research area right from its inception.

Ions are available in a myriad of shapes, sizes, and charges due to the combinations arising from the elements in the periodic table in their various oxidation states.[8] These involve many selectivity patterns with regard to potential receptors.[9] As opposed to electrons, the different natures of ions give rise to qualitative distinguishability. Their local concentration gives quantitation of the input signal. Interesting ramifications arise. For instance, molecular-scale systems[10] with multiple receptors can select different ionic inputs into the different receptors without additional guidance, i.e. the inputs are wireless. Practical distinguishability of ionic signals by molecular-scale devices without "wiring" is unparalleled in conventional electronics at any level of integration and has considerable potential for exploitation by chemically minded scientists.

Ions are the prime movers of life. Some of them are the signal carriers in the nervous systems controlling intelligence and motion in the higher life forms.[11] Even in the simplest cases, ions carry the intracellular signals which are essential for survival of the cell.[12] This involvement of ions in intelligence naturally draws designers of photoionic devices into the area of signal processing. On the other hand, spying on these ions will provide a window on some of the inner workings of life. Hence, many photoionic devices have been targeted for ion sensing in biological environments. Of course, there are beautiful examples of related devices in nature operating in the photon in–ion out mode, which is the reverse of the type discussed here, e.g. rhodopsin in retinal rods of the human eye[11,13] and bacteriorhodopsin in membranes of purple bacteria.[14]

Ions can easily serve as the "finger" on the molecular-scale light switch.[15] Due to their intrinsic charge, ions can be marshalled and directed by electric fields. Therefore, electrochemical control of local ion concentrations is feasible, especially with ultramicroelectrodes.[16] At a more subtle level, membrane potentials are capable of large modulations of local ion concentrations in microenvironments.[17] However it must be noted that both these approaches are currently limited to a scale somewhat larger than the single molecule. Nevertheless, with the advent of scanning electrochemical microscopy[18] there is hope for the future because scanning microscope probe tips routinely handle single molecules.[19] Molecule-based approaches are also available in the form of photoswitchable ion receptors,[20–26] some of which can provide ion pulses within ns timescales. Photoreleasable caged ions are irreversible versions.[27–32] A potentially powerful combination would be the excitation of these ion complexes via the probe tip of a near-field scanning optical microscope.

Photon emitting, i.e. luminescent molecules, are detectable with extreme sensitivity at the single molecule level.[33] Thus luminescence is a natural approach to the operation of devices at the molecular level. It is also notable that luminescent molecules can yield information with <nm spatial resolution (though not visualization) even without special microtechniques.[34] Luminescence output signals can be received in the human domain in various colors, i.e. multiplexing is naturally feasible. The intensity of the various colors permits quantitation of the output signals. Luminescent molecules interface smoothly with confocal microscopes[35] for 2D or 3D imaging at μm resolution and photon-scanning tunnelling[3]/near-field scanning optical[37] microscopes for 3D imaging at nm resolution. Most luminescent devices have the personal touch since they are easily tested/demonstrated at the ensemble level by visual observation. The luminescence lifetime (which can vary from ~ns to ~ms) should, in principle, allow rapid information handling, though the associated ion interactions will usually be rate-limiting. Transactions with protons over minimum distances in aqueous media will result in maximum rates, though protonic transactions in other media are also of interest.[38]

Molecular photoionic devices with switchable response,[39] at the ensemble level, display nonlinear in/out characteristics which can be operated either as analogue or digital devices by proper control of the ion concentration input variable.[40] When employed in smaller numbers, they should show "on/off" action, reminiscent of single-channel events in electrophysiology.[41]

3. WHY PHOTOINDUCED ELECTRON TRANSFER?

Since PET lies at the heart of natural photosynthesis,[42] there is a wealth of information available to device designers. Some of this data has arisen from exploratory photochemistry,[43,44] while some have their origins in artificial photosynthesis research.[45–47]

Since electrons are of rather low mass, PET rates can be extremely fast with transit times in the ps–ns range. Molecular switches where the only "moving part" is an electron are likely to be much faster than those involving nuclear motion.[48,49] Since they require ion movement, photoionic devices based on PET will operate at slower rates. However these are fast enough compared to the human timescales.

Electron transfer rates are naturally subject to molecular-scale electric fields. Therefore, ion binding to a molecule is an effective way of controlling PET within it. Since PET is an excited state deactivation pathway, the competing radiative route, i.e. luminescence, also becomes exposed to ionic manipulation. Under favorable conditions, PET rates can be much faster (10^{12} s^{-1})[50] than luminescence (10^3–10^{10} s^{-1}). At the other extreme, conditions can be arranged under which PET is effectively non-existent. Therefore, luminescence can be ionically switched between "off" and "on" states representing digital action.[40]

The transfer of an electron requires a donor and an acceptor, i.e. a multicomponent system is necessary if the process is to occur within a single molecular entity. Molecular-scale devices employing PET are therefore necessarily supramolecular. The integrity of the individual components or subunits will be best maintained if they are held together by weak associations. Nevertheless the same outcome can be largely achieved, especially for photochemical purposes, by connecting the components together with covalent σ bonds. While these can allow some degree of inter-component interaction,[51–53] this approach has been adopted by most device designers in the field mainly because robust systems result. PET-type processes are also found in mechanically interlocked systems such as rotaxanes and catenanes, especially those which rely on charge transfer (CT) interactions for their assembly.[54] It will only be a matter of time before ionically switchable luminescent devices are developed from this approach as well.[55] Overall, PET systems will continue to play a major part in the growth of supramolecular photochemistry.

4. LUMOPHORE–SPACER–RECEPTOR SYSTEMS (NORMAL LOGIC)

A large fraction of the research in ionically switchable luminescent devices is in this category. Several reviews of the early work are available.[15,39,40,56–65] Figure 1

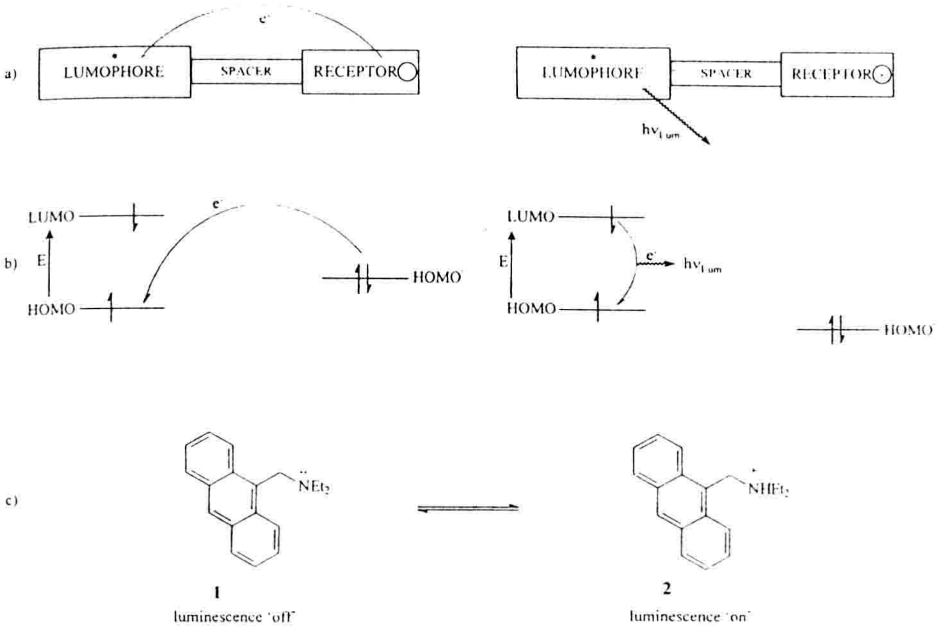


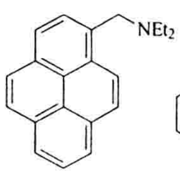
Figure 1. (**a**) Schematic representation of the three-module format of an ionically switchable photoactive dyad (normal logic). Receptors are shown throughout with a hole even though a cavity is not a prerequisite for binding a guest ion. Note that the excitation (*) in the lumophore drives the intramolecular, intermodular electron transfer which quenches the luminescence. The electron transfer may transfer along the bonds in the spacer or through space even though the latter has been chosen for reasons of clarity in all figures. The direction of the electron transfer is such that the presence of a cationic guest on/in the receptor would discourage the process (arguing at the simplest electrostatic level). Now luminescence wins the competition. (**b**) Frontier molecular orbital energy diagrams corresponding to part (**a**). Note that ground state nomenclature is used throughout this article even though the electron occupancy corresponds to the excited state of the lumophore. The intermodular electron transfer is exergonic only in the cation-free case where the HOMO' of the receptor is higher than that of the HOMO of the lumophore. The HOMO' of the receptor is stabilized upon binding the cation. Electron transfer is relatively fast (c.f. luminescence) at moderate exergonicities. (**c**) An example illustrating the principles of parts (**a**) and (**b**) from the aminomethyl aromatic family. The luminescence is switched "off" when the amine unit is unprotonated. At sufficiently high proton concentrations ($pH < pK_a$) the amine becomes protonated and the luminescence is switched "on".

summarizes the key principles of these lumophore–spacer–receptor systems along with a representative example (**1**)[39] from the aminoalkyl aromatic family. System **3**[66] is a recent example of this type where the relatively long intrinsic fluorescence lifetime of the discoidal pyrene fluorophore is used to develop a lifetime sensor for pH. Lifetime sensing[67] has an advantage over intensity sensing since no complications arise from environmental variables such as optical path length or local concentration of the sensor or quenchers. Of course, the fluorescence intensity of **3** is smoothly pH-dependent as well.

The switching efficiency of lumophore–spacer–receptor systems can be improved by using multiple receptor modules. The PET rate is increased in the device when free of guest ions since more than one site can provide the transiting electron. The simplest cases, such as **4**,[57,68] are those where the receptor units are well separated to prevent interdependent ion binding with an interposed lumophore to minimize the lumophore–receptor spacing for maximum PET rates. Besides this statistical effect, receptors may also cooperatively participate in PET.[69] This may be the case in **5**[70] and **6**.[71]

Systems with neighboring receptors tend to show multiple steps in the fluorescence intensity–pH profile since (1) the pK_a values of the neighboring receptors tend to differ considerably, and (2) receptors at different distances from the lumophore have different PET rates when they are free of guest ions. However these cases are usually designed to exploit their chelating ability towards metal ions with pH studies being of secondary interest. Systems **5**,[70] **7**,[72] and **8**[73] were aimed at Zn^{2+}, and **9**[74] raises interesting possibilities for binding a variety of inorganic and organic guests. In some of these situations, the cyclophane nature of **9** would suggest the involvement of the benzene fluorophore in a receptor role as well.

Lumophores other than hydrocarbons have been incorporated into the aminoalkyl aromatic family of ionically switchable luminescent devices. For instance, metalloporphyrin systems such as **10**[75] have been used to good advantage. These cases absorb and emit at wavelengths as long as 596 and 650 nm, respectively. Such red-shifted systems are particularly attractive for monitoring ion movements in



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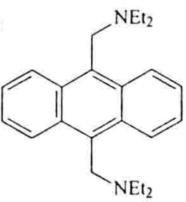

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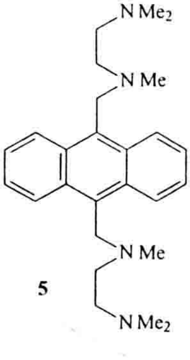

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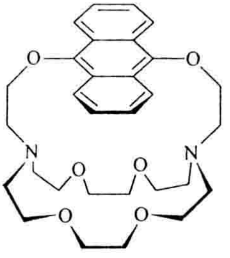

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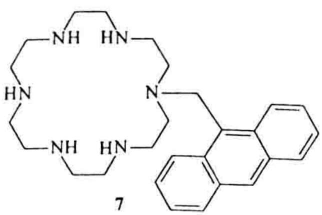

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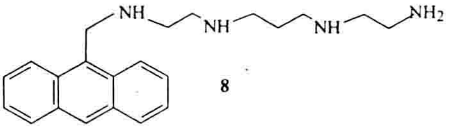

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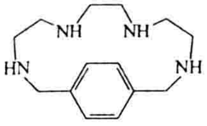

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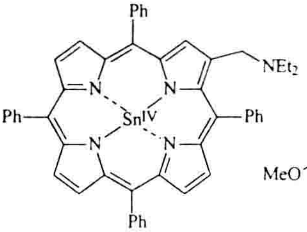

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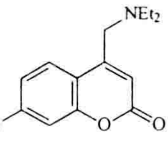

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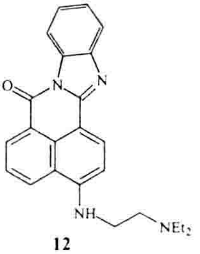

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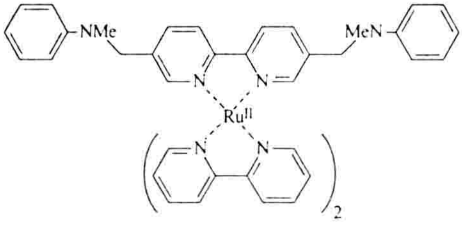

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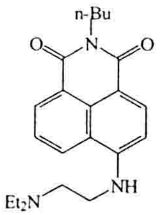
intrinsically colored biomatrices. A large addition can be made to the aminoalkyl aromatic family if we look towards heteroaromatic compounds as lumophores. This can be particularly profitable and interesting in the following way.

The PET systems of the aminoalkyl aromatic type discussed so far display a very simple behavior in that luminescence intensity (or quantum yield) is the only variable. Such systems are very user-friendly as a result and tolerate a wide variety of communication wavelengths. However these simple systems could be adapted to include an additional absorptiometric sensing channel which can confirm the results of ion density (pH say) obtained via luminescence. Of course, such increased user-confidence is only attained with a proportionate reduction in simplicity. Now excitation needs to be done at the isosbestic wavelength. These systems, e.g. **11** and **12**, use a push–pull fluorophore with electron donor and acceptor substituents which give rise to internal charge transfer (ICT) excited states.[76] In contrast, the simple PET systems employed aromatic hydrocarbon fluorophores with essentially pure $\pi\pi^*$ excited states.[68] The charge separation in ICT states can cause electrostatic interactions across the spacer with the ion-bound receptor. Thus, the absorption spectrum undergoes pH-dependent shifts. The observed emission spectrum shows much smaller shifts (if any) because only the ion-bound system is emissive in most cases. Systems **11** and **12** are important because they are dual-channel sensors using both emission and absorption. Closely related examples arise from inorganic chemistry since charge transfer is common during the excitation of metal complexes. For instance, tris(2,2′bipyridyl)Ru(II) displays an emissive excited state with metal-to-ligand charge transfer (MLCT) character. This has been built into the proton switchable system **13**.[77] However, the exploitation of heteroaromatic lumophores with ICT or MLCT excited states has to be approached carefully since they can introduce interesting kinetic effects, as the following case demonstrates.

While the thermodynamic basis for the design of ionically switchable luminescent PET devices is now well established,[39,40] the switching action is eventually controlled by the competition between the *rates* of luminescence and electron transfer. The connection between the rates and the thermodynamics is of intense current interest.[50] In the regioisomeric pairs **14** and **15**, PET sensor action is found to be sensitively controlled by kinetic factors.[78] System **14** displays strong fluorescence switching "off–on" action with protons, whereas **15** is essentially unaffected. This can be understood as being due to the dipole created in the ICT excited state attracting or repelling the transiting electron in **14** or **15**, respectively, even though the thermodynamic driving force is essentially the same. The present phenomenon is important for two additional reasons:

1. This is the first demonstration of self-regulated PET, i.e. the PET process is controlled by the characteristics of the lumophore within the working device. Self-regulation is an important aspect of self-organized molecular processes.[1]
2. PET within the photosynthetic reaction center occurs along preferentially along one of two nearly identical branches.[42] It may interest students of this modern enigma that a similar path selectivity has now been demonstrated within the much smaller supramolecular systems **14** and **15**.



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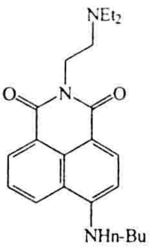

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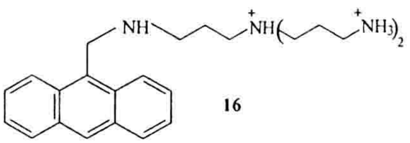

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