2013: A Small Space Odyssey with Luminescent Molecules

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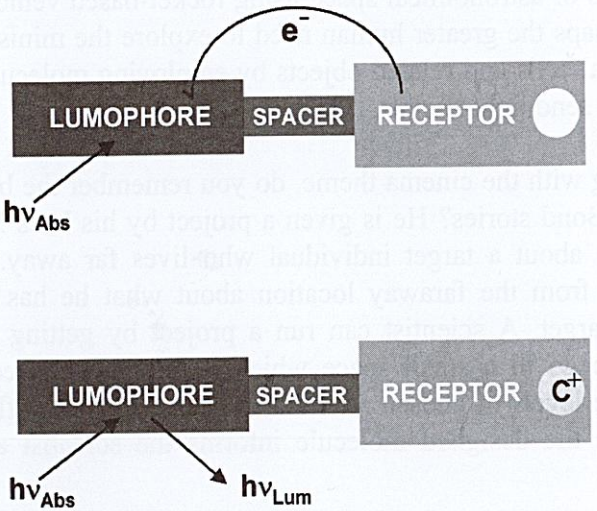
Abstract: The luminescence of molecules designed according to photochemical principles based on the 'lumophore-spacer-receptor' format can be switched between 'on' and 'off' states. More elaborate versions of the 'lumophore-spacer-receptor' format allow more complex switching patterns which satisfy Boolean logic. Due to the small size of these molecules, nanometric information handlers become possible. These can measure the concentrations of chemical species in millimetric channels and in micrometric living cells which lead to applications in medical devices and physiology respectively. Others of this type serve as identification tags on micrometric polymer beads which serve combinatorial chemistry.

'2001: A Space Odyssey' is a highlight of science fiction cinema which had a Sri Lankan connection. The screenplay was due to long-time Sri Lanka resident Arthur C. Clarke. Just like humans need to explore the vast reaches of astronomical space using rocket-based vehicles, we can satisfy perhaps the greater human need to explore the miniscule spaces of biological cells and related objects by employing molecular vehicles designed to send light signals.

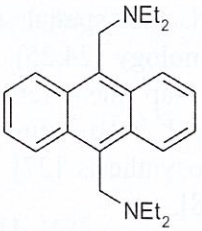
Still staying with the cinema theme, do you remember the basic plot of the James Bond stories? He is given a project by his boss M to gather information about a target individual who lives far away. Mr. Bond informs M from the faraway location about what he has discovered about the target. A scientist can run a project by getting a designed molecule to go to a small space which is humanly inaccessible and measure the levels of chosen atoms or molecules. Then a fluorescence signal from the designed molecule informs the scientist about these

levels. Molecules can indeed be designed so that they can perform chosen functions in chosen small spaces. Some of these uses take us across biology to medical diagnostics. Other potential uses take us in the opposite direction towards computer engineering.

What is the design basis of our useful molecules? Photochemistry which combines light and molecules is a good starting point. Photoinduced electron transfer (PET) is the heart of green plant photosynthesis and is a major channel of de-exciting excited states of molecules [1]. Luminescence is another such channel which is easily observed by the unaided eye. The controlled competition of luminescence with photoinduced electron transfer (PET) can switch the luminescence 'on' or 'off' by chemical means in an easy, predictable manner. The modular nature of 'lumophore-spacer-receptor' supramolecular systems is not only vital for the occurrence of PET, but also for the prediction of sensor/switch characteristics such as colours of the optical signals and the concentration range of the analyte (C^+ in the scheme below).



This leads to sensor molecules which can measure chemical species levels in small spaces [2]. Some are currently used to monitor acidic compartments in living cells as foreign matter is ingested and trafficked. [3]. In fact, these are pH sensor molecules developed three decades ago in Sri Lanka [4]. An example is shown below.



Other sensor molecules based on the principles mentioned above [5] are working in hospitals and in ambulances performing blood diagnostics [6]. They measure sodium, potassium and calcium, besides pH, carbon dioxide and oxygen. These arose from research carried out by Roche Diagnostics in collaboration with Queen's University, Belfast [7].

The luminescent PET sensing/switching principle is so general that it can be adapted to build molecular-scale information processors which employ chemical species as inputs and light as output. Wireless interfacing of molecular-scale devices to human operators thus becomes possible. These processors are far smaller than the smallest silicon-based electronic devices. A molecular computational device can be successfully operated in a sphere 3 nm in diameter [8]. Remarkably, this sphere can be found in common soap solutions. In spite of this size advantage, many difficulties hinder progress if we only follow the path of semiconductor device mimicry. Nevertheless, a whole family of molecular logic devices of increasing complexity have been built in this way [9,10], including the demonstration of molecular-scale arithmetic

operations [11]. So there has been a growing effort to use computational ideas expressed in molecules [12-16]. This work has also given us the opportunity to comment on developments in related areas [17-21]. These computing molecules can be put to new uses. For instance we have shown that some of these devices have potential uses as smart detectors, such as in the direct detection of two [22] or even three [23] analytes at once. Building identification tags for micrometric objects such as polymer beads has been a rare example of how computing molecules can exceed the spatial resolution of well-established radiofrequency ID technology [24,25]. Molecular logic gates can also be self-assembled in soap membranes for added accessibility and convenience [26]. Indeed, soap membranes have also allowed us to mimic aspects of photosynthesis [27] and have provided nanoscopic worlds for us to map [28].

Physical properties such as temperature can also be brought into the fold of luminescent sensors and switches by employing thermoresponsive polymers and polarity-sensitive lumophores [29]. Some of these are the most sensitive molecular thermometers known. They can also be tuned to suit a chosen temperature [30]. Others can respond to temperature as well as to a chemical species such as protons. Molecular logic gates are also made possible in this way [31]. Advanced techniques like fluorescence lifetime imaging microscopy can enhance the usefulness of these molecular thermometers [32].

Probably luminescent sensing and switching molecules will continue to serve fields as diverse as medical diagnostics and information processing as the 21st century progresses [33-42].

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