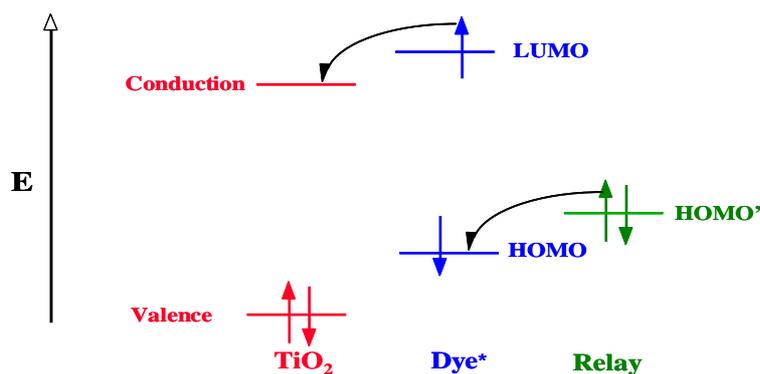


# PHOTOACTIVE MATERIALS FOR BUILDINGS

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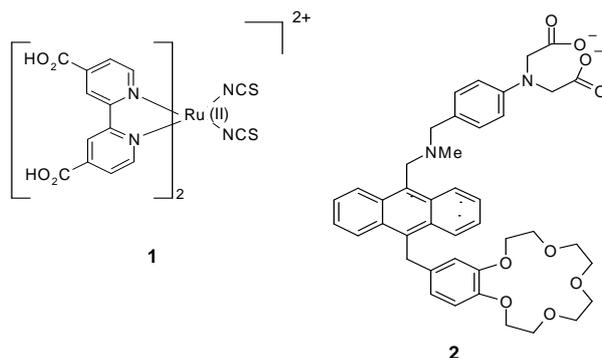
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Since the intertwining of light and electron transfer enables life on the planet, it is no surprise that the same phenomenon can serve to empower materials[1] for service in the built environment. The inexpensive generation of electrical power from sunlight in a distributed manner will probably become possible with photoelectrochemical cells embedded in windows. From a chemical viewpoint, **1** can undergo photoinduced electron transfer (PET) with TiO<sub>2</sub> and the resulting **1**<sup>+</sup> can undergo further electron transfer with electrochemical relay I, when the thermodynamic conditions are considered (Fig. 1). However, the efficiency of charge separation following PET in this and related cases is attributable to the nanostructured TiO<sub>2</sub> matrix on which **1** is bound [2]. For instance, the electric current generation efficiency in sunlight is around 1000-fold higher for **1** in nanostructured TiO<sub>2</sub> than on a chosen face of single-crystal TiO<sub>2</sub> in its anatase form[3]. Besides the hugely increased surface area of this matrix (c.f. the single-crystal), it also avoids charge-depletion layers and local electric fields near the particles. Some of these window-cells will probably be adaptable to self-cleaning tasks as well, since photoelectrochemical cells are able to decompose organic compounds via redox processes [4].

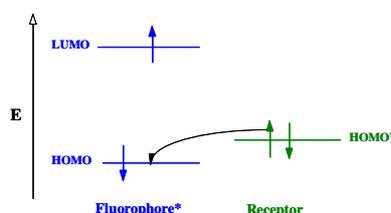


**Fig. 1:** Energy diagram for the frontier orbitals/bands of a 'TiO<sub>2</sub>-dye-electrochemical relay' system which makes up the heart of dye-sensitized photoelectrochemical cells.

When the sun goes down, the conceptual reversal of PET can provide a way of electrical light generation. Organic light-emitting diodes of nanometric thinness and very large area provide an efficient way of approaching this goal, especially those with emitter-layers in each of the primary colours with carefully engineered thicknesses to prevent losses in the internally generated photons before they escape to the outside [5]. The internal space of buildings for work and play can be enhanced with screens on which information may be displayed by adapting the same materials.

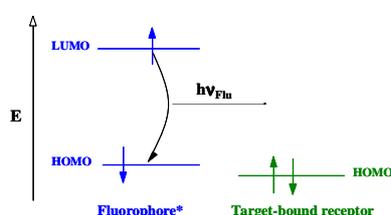


Sustainable built environments are particularly useful if people live sustainable lives inside. Detection of health conditions on a do-it-yourself basis will allow concerned people to consult a medical professional for a more thorough evaluation, somewhat like current pregnancy tests. A home equipped with such testing facilities would be a particularly comforting environment to live in. PET can be marshalled to help in this situation too, by being built into sensors and diagnostic systems. These show how medical applications arise from the emulation of computational ideas with molecules. The thermodynamic situations which are encountered during the competition between PET and fluorescence are shown in Figures 2 and 3.



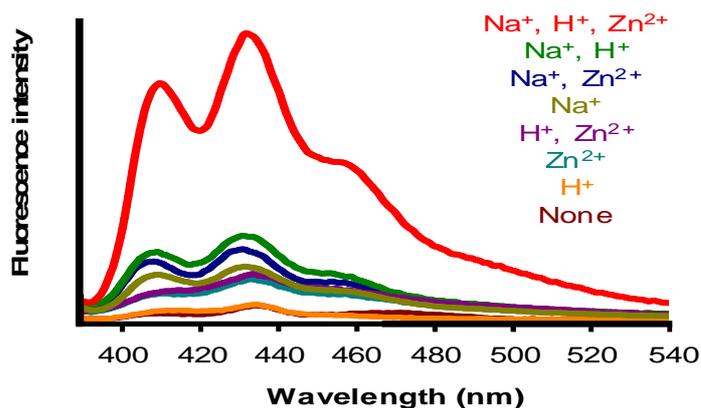
**Fig. 2:** Energy diagram for the frontier orbitals of a ‘fluorophore-spacer-receptor’ system which makes up the heart of fluorescent PET sensors and logic devices.

For instance, Boolean diagnostic system **2** [6] involves three thermodynamically allowed PET processes arising from each of the receptors - tertiary amine, benzo-15-crown-5-ether, and phenyliminodiacetate targeting  $H^+$ ,  $Na^+$  and  $Zn^{2+}$  respectively. The latter three species form the targets involved in the diagnosis. All three PET processes need to be stopped before the fluorescence output has a chance of being released at a ‘high’ level. As each receptor is bound by its corresponding cation, the PET processes are shut down one by one due to electrostatic attraction between the cation and the transiting electron.



**Fig. 3:** Energy diagram for the frontier orbitals of a ‘fluorophore-spacer-receptor’ system when the receptor is bound to its target.

The simultaneously ‘high’ concentrations of three biologically important cations are signalled by the emission of a light signal which is easy to see (Fig. 4). In the present context, the adjective ‘high’ means that the cation concentration is large enough to tip the ratio of bound-receptor to free-receptor within **2** to significantly above 1. In chemical design terms, this means that the target concentration is significantly larger than the reciprocal of the receptor-target binding constant. The latter can be chosen to match the target concentration present in the blood, say, of a healthy person. So **2** can be seen to go some way towards easily indicating electrolyte excess and hence, renal dysfunction. The difference with **2** and its cousins [7-9] is that multiple analytes are evaluated simultaneously according to a small, but non-trivial, algorithm. Rudimentary versions of **2**, each responding to a single target are currently used worldwide on a substantial scale [10].



**Fig. 4:** Fluorescence emission spectra for a 'lab-on-a-molecule' system when it is interrogated with various target combinations.

## References

1. Electron Transfer in Chemistry. Vol 5 (Eds. V. Balzani, A.P. de Silva and E.J. Gould) Wiley-VCH, Weinheim, Germany, 2001.
2. M. Gratzel, Nature 2001, **414**, 338.
3. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Gratzel, J. Am. Chem. Soc. 1993, **115**, 6382.
4. A. Y. Zhang, M. H. Zhou, L. Liu, W. Wang, Y. L. Jiao and Q. X. Zhou, Electrochim. Acta 2010, **55**, 5091.
5. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, Nature 2009, **459**, 234.
6. D. C. Magri, G. J. Brown, G. D. McClean and A. P. de Silva, J. Am. Chem. Soc. 2006, **128**, 4950.
7. D. Margulies and A. D. Hamilton, J. Am. Chem. Soc. 2009, **131**, 9142.
8. T. Konry and D. R. Walt, J. Am. Chem. Soc. 2009, **131**, 13232.
9. J. Halamek, J. R. Windmiller, J. Zhou, M. C. Chuang, P. Santhosh, G. Strack, M. A. Arugula, S. Chinnapareddy, V. Bocharova, J. Wang and E. Katz, Analyst 2010, **135**, 2249.
10. J. K. Tusa and H. He, J. Mater. Chem. 2005, **15**, 2640.