

Review

Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors

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Abstract

This review article focuses primarily on the work carried in our laboratories over the last few years using luminescent and colorimetric sensors, where the anion recognition occurs through hydrogen bonding in organic or aqueous solvents. This review begins with the story of the discovery of fluorescent photoinduced electron transfer (PET) sensors for anions using charged neutral urea or thiourea receptors where both fluorescent and NMR spectroscopic methods monitored anion recognition. This work led to the development of dual luminescent and colorimetric anion sensors based on the use of the ICT based naphthalimide chromophore, where ions such as fluoride gave rise to changes in both the fluorescence and the absorption spectra of the sensors, but at different concentrations. Here, the former changes were due to hydrogen bonding interactions, whereas the latter was due to the deprotonation of acidic protons, giving rise to the formation of the bifluoride anion (HF₂⁻). Modification of the 4-amino-1,8-naphthalimide moiety has facilitated the formation of colorimetric anion sensors that work both in organic or aqueous solutions. Such charge neutral receptor motifs have also been incorporated into organic scaffolds with norbomyl and calixarene backbones, which have enabled us to produce anion directed self-assembled structures.

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1. Introduction

The development of luminescent signaling systems and devices, such as switches, sensors and ‘nano-machines’ is an active area of research in organic and inorganic supramolecular photochemistry [1,2]. Examples of such signaling molecules or arrays of molecules, have been constructed from purely organic chromophores/lumophores, inorganic metal ion frameworks, coordination frameworks, or by the suitable combination of any of these. This gives rise to rich varieties of structural-chemical motifs where the luminescence signaling can be stimulated or generated, by light energy, *e.g.* by direct excitation, or *via* energy or electron transfer processes in donor–acceptor arrays, electrochemically or by chemical inputs, such as ions or neutral molecules. The discovery of the latter paved the way for the development of chemical sensors [3,4], which have been found to be of major importance in: (i) industry (for monitoring chemical processes, pollution, *etc.*); (ii) diagnostic and therapeutic medicine (for monitoring electrolytes, in critical care analysis and as therapeutics in photodynamic therapy, *etc.*); and (iii) various kinds of environmental monitoring.

In general, the criteria behind chemical sensing have involved the design of small single molecules that specifically recognize a single ion or a molecular species in a competitive media in a reversible manner and in a given concentration range. For continuous monitoring the need for reversibility is an essential requirement. However, in the case of once-off measurements, such as the analysis of blood and serum samples or glucose monitoring, such reversibility is not always necessary [5]. Moreover, single analyte sensing is possibly giving way to a new class of sensors that detect classes or mixtures of chemicals in a similar manner to which nature has developed human taste buds or other receptors such as those for detecting smells [6]. Nevertheless, single analyte detection is still of significant importance, particularly for understanding various physiological processes. Hence, Zn(II) is believed to play a pivotal role in many extra- and intracellular physiological functions which can only be monitored or observed *in vitro* by using single-ion selective sensors [7]. The same may be said for many organic and inorganic anions, whose role in nature is often well understood, but has been difficult to explore by real-time monitoring using non-invasive methods. Anions are essential to life, as many biological processes depend on the presence or transport of anions, or use anions to carry out chemical transformations. They are also important for many industrial processes and are often found as harmful pollutants [8]. Consequently, the need for developing anion sensors for complex media such as in blood, serum, cells, soil, freshwater, *etc.* is of utmost importance. For such sensing, single molecular sensors are ideal, provided that a clear selectivity and sensitivity can be achieved. For such, the same design strategies can be employed as have been used in the development of sensors for cations, an area that has been well explored over the last two decades [9]. Examples of such strategies include the use of ion or molecular receptor moieties as an integrated part of a signaling unit (either luminescent or colorimetric) or where a short spacer, with the aim of minimizing any ground state

interactions, separates the two units. The latter is an example of the so called photoinduced electron transfer (PET) sensors, which were originally developed independently by de Silva and Czarnik, and have been employed in many excellent examples since [10,11]. Other alternative design strategies such as the displacement assays, as developed by Anslyn and coworkers, has also been developed [12]. Irrespective of the design strategy, the recognition event involves the binding of the analyte to the receptor and in all cases induces some changes in the physical properties of the receptor. These in turn give rise to concomitant changes in photophysical properties such as absorption or emission wavelength, intensity, quantum yield, lifetimes, polarization, *etc.*, all of which can be employed to quantify the analyte concentration, or monitor its movement in real-time [13,14].

In the past 8 years, we have focused a facet of our research effort on the development of sensors for cations, using colorimetric or fluorescent PET or lanthanide luminescent sensors [15]. At the same time our interest in developing sensors for anions capable of detecting selectively a single ion using the changes in the various aforementioned photophysical properties also began [16]. Unlike the sensing of cationic ions and molecules, and even though the sensing of anions dates back to the late 1960s, anion recognition has been generally more difficult to achieve and only in the last decade or so has it become a ‘popular’ area of research, with large numbers of new publications and reviews having been published in this field in the last few years [17–20].

Our interest in anion sensing derived from the fact that, to the best of our knowledge, no anion PET sensors had been developed using charge neutral receptors where the anion recognition occurred through hydrogen bonding. Even though many elegant PET sensors had been developed for Groups I and II cations, transition metal ions, ammonium ions and even for anions, such as phosphates and pyrophosphate using charged ammonium moieties as receptors, the luminescent sensing of anions using charge neutral receptors had been largely unexplored [21]. This can in some ways be explained by the complex nature of the anions, which by definition: (i) have lone pairs of electrons (usually); (ii) possess high Lewis basicity; (iii) exhibit a wide range of geometries that can often be highly pH dependent (therefore the construction of complementary receptors necessitates a higher measure of design); and (iv) high solvation energies. Nevertheless, examples of luminescent anion sensors have emerged from the laboratories of Sessler and coworkers [22], Anslyn and coworkers [23], Gale [24], Parker and coworkers [25], Fabbrizzi [26], Beer [27] and many others. Inspired by their work, we set out to develop sensors that: (i) were designed on the PET principle; (ii) would be highly luminescent in either the presence or absence of anions; (iii) would emit at long wavelengths; (iv) could be made in a facile manner using few step synthesis; and (v) would bind the anion in a reversible manner using hydrogen-bond donor receptors. The work by Schmidtchen [27], Davis and Joos [28], Schneider [29], Umezawa [30], Hamilton [31], to name just a few, had established that functional groups such as urea, thiourea and guanidinium all bind anions through linear hydrogen bond-

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