

14th International Conference on Nanomaterials and Nanotechnology, March 30-31, 2017 | Madrid, Spain- Luminescence chemosensors based on polythiophene and Covalent Polymers Containing Discrete Heterocyclic Anion Receptors

Mustafa Musa Jaber Alshamkhee

Al-Nahrain University, Iraq

This contribution reports the synthesis and post-polymerization modification of highly regioregular polymer precursor poly[3-(6-bromohexyl)thiophene] (PHT-Br), prepared by nickel-catalyzed Grignard metathesis polymerization (GRIM). Modification of PHT-Br into corresponding cationic polyelectrolytes using simple quaternization reaction with tributylamine or tributylphosphine respectively was used as the first approach for introducing functionality allowing sensing of selected metal ions. Used procedure allowed preparation of luminescent conjugated polyelectrolyte bearing simultaneously both phosphonium and ammonium pendant groups in the same polymer mainchains. Transformation of pendant bromide groups into azides ones followed by Huisgen 2+3 dipolar cycloaddition ("click" reaction) with luminophore N-(prop-1-yne-3-yl)-4-(morpholine-1-yl)-1,8-naphthalimide coded as NF was used as a second approach. Luminescence quenching has been evaluated quantitatively using Stern-Volmer methodology (using potassium ferrocyanide and ferricyanide as model pollutants). Polyelectrolyte-approach appeared promising although it is worth to mention a partial lack of selectivity. Clickbased approach increased the sensor selectivity. Although free NF provided high luminescence yield (around 80%) as well as parent polythiophene (18% luminescence quantum yield) product of "click" reaction exhibited only 4% of quantum luminescence yield. This observation represented a main drawback of "click" approach. In contrary sensing abilities of naphthalimide-based polythiophene increased

about two orders. The field of polymer chemistry has made tremendous progress since Staudinger first pioneered various polymerization methods in the early 1920's. Staudinger proposed structural formulae for natural rubber, polystyrene, and polyoxymethylene, and is also credited with coining the term "macromolecule" which is still commonly used today. The field of synthetic polymers was advanced further in the 1930's when Carothers developed two widely used synthetic polymers, neoprene and nylon. The importance of these materials cannot be overstated. For example, nylon and other polyamides are excellent fiber forming materials, and were initially used to make ropes, parachutes, and tents, but applications have since greatly expanded and these and other synthetic polymers can now be seen in almost all aspects of everyday life. This ubiquity has spawned wide-spread efforts to develop new and improved materials. A few areas of advanced focus within this general paradigm include creating synthetic replacements for biological tissues and developing macromolecular materials suitable for use in diagnostic and array technologies.

Another major thrust in polymer chemistry has come from the field of "supramolecular chemistry", a term coined by Lehn to mean chemistry beyond the molecule. As chemists began to exploit the weak non-covalent interactions (which represent the foundation of supramolecular chemistry) to create new molecular receptors and chemosensors, it soon became apparent that the same principles could lead to advanc-

es in the field of polymer chemistry. A major subset of this latter effort has been devoted to the synthesis of so-called main-chain supramolecular polymers, where reversible/dynamic non-covalent interactions within the polymer backbone are used to assemble monomers into larger polymeric structures. Separate from this, a number of researchers began to realize the potential benefits of incorporating small molecule supramolecular receptors into polymeric structures. The vast majority of these latter systems consist of conjugated polymers containing receptors for positively charged or neutral species. One highly utilized approach involves the incorporation of crown ether species for metal ion recognition and sensing. For example, Swager reported how an appropriately designed, conjugated polymer chemosensor containing crown ethers would undergo recognizable changes as the result of potassium induced aggregation.

In spite of the above advances, it was only recently that the number of polymers that incorporate receptors for anionic species began to increase. This tardiness in terms of materials development is somewhat surprising given the role anionic species play in the environment and in biological processes. It is now well recognized that many anionic species, such as fluoride, nitrate, phosphate, and cyanide, constitute major environmental pollutants; there is thus a clear, widely appreciated need for materials capable of recognizing, capturing, and detecting these and other anionic species. Furthermore, excesses in phosphate anion levels in patients suffering from end-stage renal failure is a frequent complication that can lead to a disease state known as hyperphosphatemia. In most cases dialysis in combination with ingestible anion exchange resins is used to control the level of phosphate in the blood. However, neither of these methods is fully satisfactory, in part because the underlying methodologies are not phosphate selective. The authors thus believe that new materials, such as anion-specific dialysis membranes, could be used to control phosphate anion concentrations for patients on dialysis and lead to clinical advances. The incorporation of supramolecular receptors specific for an-

ionic species into polymeric frameworks represents a first step towards achieving this long-range goal. Related anion-binding macromolecules could also see application in the recognition and sensing of anions of environmental concerns and in the areas of separation and purification. Taken in concert, these various potential benefits provide an incentive to prepare anion receptor-modified polymers. The goal of this chapter is to provide a summary of recent work in the area.

To the best of our knowledge, no reviews have appeared that cover the chemistry of macromolecular systems targeting the problem of anion recognition. The focus of this chapter will be on polymeric systems that incorporate heterocycle-based anion receptors into polymeric structures. Heterocyclic receptors as additives to polymers for applications such as polyelectrolyte development, will be covered, as will be polymers that contain anion receptors either as pendant side-chains or incorporated directly into the polymer main-chain. As will become apparent from the present review, the majority of the systems that exist today are conjugated polymers that have been applied as so-called chemosensors. However, it is our hope and expectation that a detailed description of these and related systems will inspire the synthesis of new and improved systems for anion detection, sequestration, extraction, and separations, among other conceivable applications. According to the principle of Occam's Razor, "entities must not be multiplied beyond necessity," which one can interpret to mean that often the simplest explanation is the correct one. Analogously, in engineering and materials science, one attempts to get the biggest bang for one's buck by using cheap and simple materials to build up complexity and solve pressing problems. Over-complicated syntheses or expensive starting materials can lead to greatly diminished returns and harpoon the chances that the molecule or material will ever see wide-spread application. Such appreciations may well have inspired early researchers working at the interface of anion recognition and polymer research.