



Insights into the anion effect on the self assembly of perylene bisimide diimidazolium salts



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ABSTRACT

We studied how changing the anion affects the self-assembly of three diimidazolium salts bearing a perylene bisimide spacer. In particular we used $[\text{BF}_4^-]$ and $[\text{NTf}_2^-]$ based salts together with a mixed salt bearing both $[\text{I}^-]$ and $[\text{BF}_4^-]$ anions. Thermal as well as concentration and temperature dependent spectroscopic investigations revealed that changing the anion impacts on solid state and solution aggregation, leading to articulate thermotropic behaviors and contrasting solvent effects, respectively. We also studied the electrochemical behavior of the salts to verify if changing the anion alters the redox properties of the salts. Finally, different anions also lead to very different aggregate morphologies, as evidenced by SEM and TEM measurements.

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1. Introduction

Many functional materials owe their applications to the properties emerging from the formation of ordered, well defined structures and domains originated by the self assembly of suitable small molecules [1,2]. Self-assembly is the spontaneous association of these building blocks governed by different blends of non-covalent forces such as hydrogen bonding, π - π stacking, van der Waals and Coulombic interactions. Their concomitant and cooperative action, associated with their strength or different directionality dictates to a large extent the characteristics of the materials obtained.

Ideally, such simple molecules should be readily synthesized and easily endowed with functional moieties able to impart them propensity to self assemble or stimuli responsiveness [3].

Recent years have witnessed an intense focus on the self assembly of π -conjugated molecules characterized by a suitably extended π -surface area. In this regard, perylene bisimides (PBIs) meet most of the criteria described above [4,5]. Such molecules possess indeed high thermal and photochemical stabilities which are required for optoelectronic applications. Moreover their strong

emission in the visible range and near to unity quantum yields are fundamental for their use as fluorescent sensors [6], in bioimaging [7] or organic photovoltaic devices [8–10]. Since PBIs are resistant to oxidation and exhibit n-type semiconductor behavior, they provide a useful tool for the construction of organic field effect transistors [11]. Finally, their well defined redox behavior has been successfully exploited to carry out important synthetic transformation as the electroreductive indirect coupling of aryl halides in mild reaction conditions and good yields [7].

It is important to highlight that the morphology of the materials determines to a large extent the properties and consequently, their applications and performances. For instance, while 3D-bulk phase materials are mainly used for thermoelectric applications, 1D-nanostructured ones find major applications in optoelectronic nanodevices [4]. The morphology of the materials is in turn heavily dependent on the chemical structure of the monomer. In light of this, the morphology of PBI-based self assembled materials can be effectively varied by introducing substituents or functional moieties both in the imide positions or on the perylene core.

Another powerful tool to modulate the properties of self assembled materials is provided by the use of charged building blocks, which enables harnessing the ionic self assembly approach [12,13].

In general, organic salts have proven useful monomers for the construction of supramolecular assemblies [14,15]. Their main advantages lie in the high thermal stability and the straightforward

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way of affecting the outcome of the self assembly process, simply by changing the nature of the cation or the anion. Moreover, the materials obtained, being ionic in nature, are often conductive which is vital in their use as components for solar cells or photovoltaic devices. Organic salts featuring perylene nuclei often behave as supramolecular amphiphiles and have proven suitable to extend their convenient optical properties to aqueous solutions where neutral PBIs are practically insoluble [16,17]. Moreover, ionic PBIs can establish interactions with nucleic acids, proving useful for DNA/RNA sensing [18] and some of them have also shown promising antitumoral activity [4] or allowed efficient gene transfection [19].

In the framework of our interest in the properties of organic salts [20], in the last years we have studied the self assembling ability of diimidazolium salts bearing an aromatic spacer between the cationic heads. By introducing subtle changes in the structure of the anion or the cation as well as varying the π -surface area of the aromatic spacer we have been able to obtain supramolecular hydro- [21], organo- and ionogelators [22], and emissive supramolecular polymers [23]. More recently, we have studied the self assembling ability of diimidazolium salts endowed with perylene- [24] and naphthalene diimide spacers [25]; these salts conjugate two well-known aggregation motifs such as the polycyclic aromatic imides and those of imidazolium salts, underpinned mainly by π -stacking, hydrogen bonding, and van der Waals interactions [26]. In both cases we observed a marked influence of the alkyl chain length and the nature of the solvent on the formation and morphology of the aggregates. As already said, when organic salts are used as building blocks of self assembled materials, changing the anion can offer a further degree of control on the properties of the material obtained and, in turn on their potential applications. Such an approach has been successfully exploited in different aggregating systems leading to anion dependent morphologies in supramolecular hydrogels [27], to changes in the aggregation mode [28] or in the optical properties [29], with enhanced emission in the solid state [30]. Although studied and applied for a diverse range of organic salts, the effect of the anion nature on the aggregation has been less investigated for PBI salts. That brings us to the question: is changing the anion of PBI salts a viable way to obtain self assembled materials with different properties? Bearing this in mind we investigated how changing the anion affects the self assembling ability of three *N,N'*-bis(3-octyl-1-ylpropylimidazolium)perylene bisimide diimidazolium salts bearing anions differing in size, shape and hydrogen bond accepting ability (Chart 1). To further probe the anion effect we also studied a double salt constituted by two

different anions sharing the same cation. The reason for this lies in the possibility of imidazolium double salts to behave in a markedly different way from the parent salts, particularly when anions with different size are involved. Such finding have been observed with imidazolium ionic liquids with respect to physical and reactivity related properties [31–33]. It can be therefore interesting to evaluate if analogous outcomes can be found when the self assembling ability of imidazolium double salts is taken into account. To the best of our knowledge this is one of the few studies addressing this issue. All the salts feature an octyl side chain in the imidazolium moieties, which was previously shown to yield the most stable aggregates when the effect of the alkyl chain length was studied [24].

Firstly, we investigated the thermal properties of each salt by differential scanning calorimetry (DSC). To assess the possible application of our salts as electroactive materials, we studied the redox properties of our salts by cyclic voltammetry on the grounds of the good electrochemical response obtained by some of us investigating the anion effect on the electrochemical properties of some imidazolium salts [34]. Then we studied the formation of aggregates in solvents of different polarity by means of concentration- and temperature dependent fluorescence and UV-vis measurements. The morphology of the aggregates was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements. Finally, comparing the results obtained in this work with those collected by us on an analogous salt bearing the iodide anion [24] will allow us to obtain a wider picture on the effect exerted by the anion on the self assembly of diimidazolium functionalized PBI salts.

2. Experimental

2.1. Materials

Commercial perylene, perylene-3,4,9,10-tetracarboxylic dianhydride, 1-iodooctane, 1-(3-aminopropyl)imidazole, sodium tetrafluoroborate, lithium bis(trifluoromethane)sulfonylimide, *N,N*-dimethylformamide, acetone, were used without further purification. Spectroscopic grade chloroform, acetonitrile, tetrahydrofuran, 1,4-dioxane and ethyl acetate were used for all UV-vis and fluorescence spectroscopy measurements. Dichloromethane was distilled before use. *N,N*-dibutylperylene bisimide (**5**) [35] and *N,N'*-bis(3-octyl-1-ylpropylimidazolium)perylene diimide diiodide salt (**2**) [24] were prepared according to reported procedures.

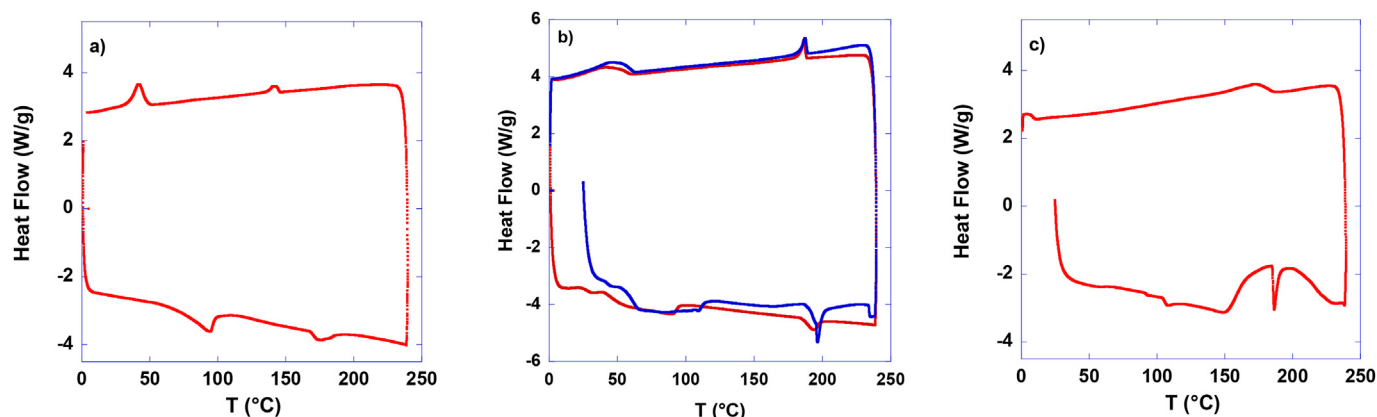


Fig. 1. Heat-cool cycles of a) **3-BF₄**, b) **3-NTf₂** and c) **3-I-BF₄**. Exothermic transitions point upwards.

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