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# Synthesis, Characterization and Aggregation Behaviour of Room Temperature Ionic Liquid Based on Porphyrin-trihexyl(tetradecyl)Phosphonium Adduct

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**Abstract:** A room temperature ionic liquid (RT-IL) made by the negatively charged water soluble meso-tetrakis(4 sulfonatophenyl)porphyrin (TPPS<sub>4</sub>) and the positively charged trihexyl(tetradecyl)phosphonium (CYPHOS<sup>®</sup> IL 101) has been synthesized and fully characterized by NMR, MALDI-TOF, differential scanning calorimetry and thermogravimetric analyses. Moreover, the growth of nanosized porphyrin J-aggregates have been induced in solution through the "in situ" photogeneration of HCl acid in chlorinated solvent as well as the addition in solution of a strong chiral acid. In this latter case supramolecular chiral induction has been observed on the resulting emissive nanosized aggregates. The data reported clearly evidence the central role of trihexyl(tetradecyl)phosphonium (THTDP) counter-cation in i) determining the monomeric nature of the adduct in chlorinate solution, and ii) in limiting the size of the aggregates on a nanometric scale.

## Introduction

In the last decade, the ionic liquids (ILs), developed from more than one hundred years, have been largely investigated, focusing on the improvement of their intrinsic properties, such as wide liquid ranges, good thermal, chemical and electrochemical stability, optical transparency, and low volatility.<sup>[1-3]</sup> Due to these peculiar features, mainly related to the molecular structures of the constituting anionic and cationic species, ILs have found several technological applications in different fields, such as green chemistry, electrochemical devices, biocatalysis and bioelectronics.<sup>[1-6]</sup> Moreover, ILs hybridization and/or gelation and anchoring to suitable matrices such as nanotubes,<sup>[7, 8]</sup> graphene,<sup>[9]</sup> or organic aggregates<sup>[10]</sup> significantly improve their functionalities and processing capabilities. Furthermore, ILs are recognized as ideal electrolytes in dye synthesizer solar cells (DSSCs), highly promising alternative to conventional photovoltaic devices. It is worth noting that DSSCs based on ILs instead of volatile solvents, showed lower efficiency but higher stability overtaking the poor durability of these devices mainly due to the intrinsic volatility of organic solvents.<sup>[11, 12]</sup> Organic chromophores such as porphyrins derivatives have been largely exploited as natural mimetic systems in novel photovoltaic and photocatalytic devices.<sup>[13-16]</sup> The intrinsic advantages of this class of dyes are the rigidity of their molecular structures, the large absorption coefficients in the visible region and the

possibility to tune their photophysical properties through a careful choice of peripheral substituent groups and inserted metal ions. Furthermore, in analogy with natural antenna systems, porphyrins are able to self-arrange in well-defined structures. In particular, the water soluble meso-tetrakis(4 sulfonatophenyl)porphyrin (TPPS<sub>4</sub>) has been extensively investigated as model system for exploring the structural basis of photophysical properties in excitonically coupled light-harvesting assemblies.<sup>[17-19]</sup> Indeed, the diacid form of TPPS<sub>4</sub> depending on concentration,<sup>[20]</sup> pH, ionic strength<sup>[21]</sup> and the specific microenvironment<sup>[22]</sup> is able to self-assemble into highly ordered J-aggregates. These latter, due to their intrinsic structure, reveal remarkable nonlinear optical and optoelectronic features.<sup>[23-25]</sup> Recent investigations point on the capability to induce chirality into porphyrin J-aggregates through both chemical<sup>[26, 27],[28],[29-32]</sup> and physical chiral perturbations,<sup>[33-35]</sup> or through spontaneous symmetry breaking.<sup>[36]</sup> Chirality in TPPS<sub>4</sub> J-aggregates manifests itself through the induction of exciton bands in circular dichroism (CD) spectra<sup>[36, 37]</sup> whose shape and magnitude are strictly related to the experimental conditions.<sup>[36, 38, 39]</sup> Although many reports have been devoted to aggregation phenomena in aqueous or mixed aqueous-organic phase, very few investigations deal with low polar environments<sup>[40-42]</sup> as well as complex and confined environments.<sup>[43-48]</sup> Therefore, the behavior of porphyrins in ILs<sup>[12, 49, 50]</sup> is of considerable interest especially for their potential involvement in ILs based solar cells. Indeed, imidazolium-ILs are able to induce TPPS<sub>4</sub> aggregation in water<sup>[51-54]</sup> as well as to modify the photophysical properties of model metalloporphyrins<sup>[55]</sup> simply by acting on medium polarity. Furthermore, the occurrence of supramolecular chirality in these TPPS<sub>4</sub> aggregates has been reported although all the components are achiral.<sup>[53]</sup> In comparison to other ILs, phosphonium ionic liquids (PILs) have received much less attention than the corresponding ammonium ILs,<sup>[56]</sup> although they exhibit better electrochemical and thermal properties promising for their potential applications in electronic devices.<sup>[57]</sup> PILs do not possess acidic protons, so achieving stability towards nucleophilic and basic conditions. These properties make them good candidates as green solvents in organic synthesis or in separation techniques.<sup>[58]</sup> Among PILs, the trihexyl(tetradecyl)phosphonium chloride (CYPHOS<sup>®</sup> IL 101) is traditionally used in hydrometallurgy and in separations techniques, and it has lately been explored as extracting phase for Co(II)/Ni(II) separation.<sup>[59]</sup> More recently, triisobutyl(methyl)phosphonium tosylate (CYPHOS<sup>®</sup> IL 106) has

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