

Electronic Supplementary Information for:

Micellar dye shuttle between water and an ionic liquid

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TEM investigation of PEtOx₆₇-*b*-PNonOx₃₃ nanocarriers in ionic liquid

The relatively large size of the spherical nanocarriers observed in Figure S1 suggests that the self-assembled structures may correspond to the overall size of the nanostructures (core and corona) and that, in this specific case, the IL (BMI-CF₃SO₃) may be trapped only in the coronas of the nanocarriers (since PNonOx is known to be poorly soluble in BMI-CF₃SO₃ and BMI-PF₆)^A in resulting in a relatively good resemblance between the observed sizes by TEM and the sizes obtained by DLS (Table S1) (see below for a detailed discussion related to this assumption). Since the size of the block copolymer nanocarriers is in approximately the same size range in BMI-PF₆ and BMI-CF₃SO₃ (Table S1) it may be concluded that the self-assembled nanostructures in BMI-PF₆ are also spherical nanostructures with large swollen coronas.^A

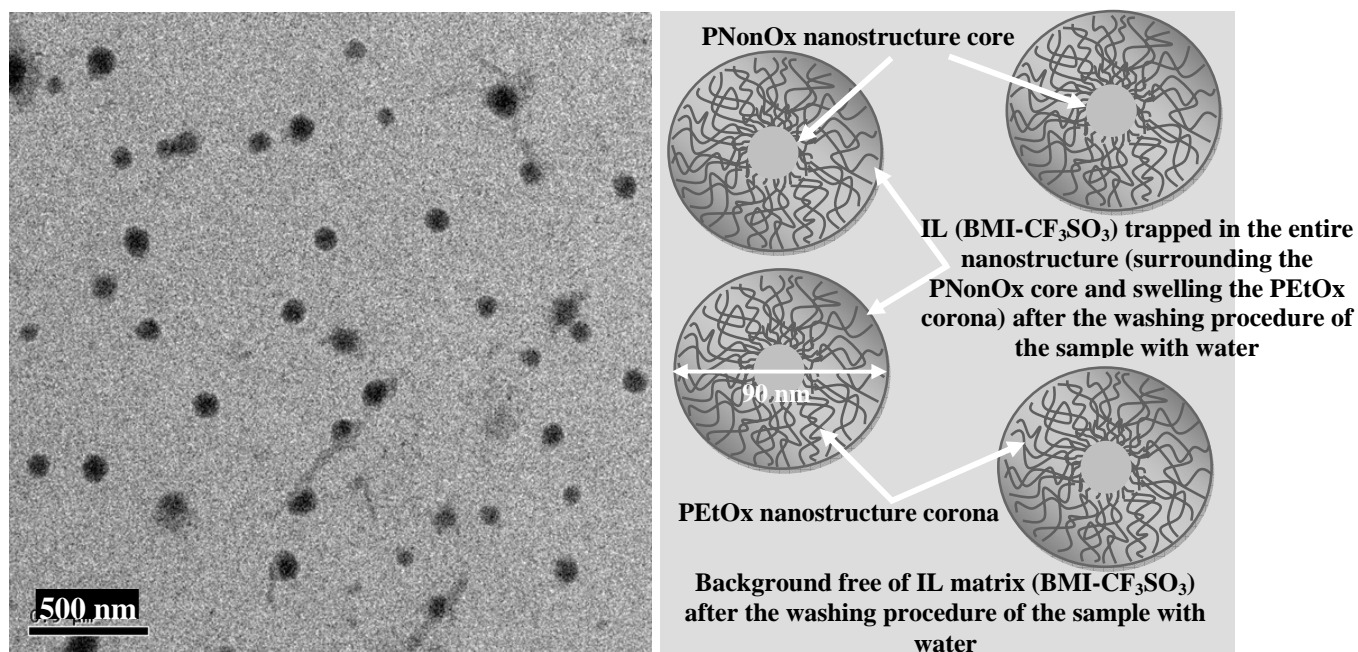


Figure S1

Table S1

| Block copolymer | Mn (kDa) | IL | D_h (nm) |
|---|----------|-------------------------------------|------------|
| PEtOx ₆₇ - <i>b</i> -NonOx ₃₃ | 12.9 | BMI-PF ₆ | 118 |
| PEtOx ₆₇ - <i>b</i> -NonOx ₃₃ | 12.9 | BMI-CF ₃ SO ₃ | 84 |

Additional considerations for TEM of the nanocarriers in BMI-PF₆

The relatively high viscosity of most of ILs as well as their negligible vapor pressure^{B,C} complicates the characterization of block copolymer micelles and nanostructures prepared in these solvents by established cryogenic TEM techniques,^{B,D} which can become a very difficult and time consuming procedure. In order to facilitate the determination of the sizes in block copolymer nanocarriers prepared in ILs by microscopic techniques, an alternative sample preparation procedure for the TEM analysis of these nanostructures at room temperature and dry conditions was utilized in this work. This alternative procedure makes use of the miscibility/immiscibility properties of ILs with the investigated block copolymer materials and with other conventional solvents to facilitate the preparation of the sample to be analyzed under the microscope at room temperature conditions (and avoiding cryogenic conditions). Hence, for the analysis utilized in this work, the nanostructures in dispersion in BMI-CF₃SO₃ was placed directly on a TEM grid followed by a washing step with a proper conventional volatile solvent, water in this specific case, in order to remove excess of BMI-CF₃SO₃ but at the same time keeping the micellar structures on the grid intact. Thus, water fulfills the following requirements for the investigated system: It solubilizes the utilized IL (BMI-CF₃SO₃) and facilitates its removal, and it is a thermodynamically compatible solvent for the coronal polymer chains (PEtOx) but an incompatible one for the core-forming polymer chains (PNonOx). In this particular case, water washes off the excess of IL (BMI-CF₃SO₃) and, at the same time, keeps the structure of the nanostructures intact. Thereafter, water was removed under vacuum and the dried nanostructures can be analyzed at room temperature conditions by TEM (or atomic force microscopy (AFM)). The TEM micrograph obtained by utilizing this approach can be observed in Figure S1 (left). Figure S1 reveals the presence of spherical nanostructures of about 90 nm in size. Note the absence of a dark background in this micrograph (as compared to other experimental procedures previously reported^{B,D}) due to the removal of the IL matrix (after washing with water). The relatively large size of the spheres observed in Figure S1 suggests that they correspond to the overall size of the nanostructures (core and corona) and that, in this specific case, the IL (BMI-CF₃SO₃) is trapped inside the corona of the nanostructures (and also surrounding the core) as conceptually depicted in

the right hand-side of Figure S1. In fact, the formation of highly viscous gel-like composites (*i.e.*, solid-like compounds or ion gels) have been observed when polymeric materials (*e.g.*, PEtOx or PEG) are dissolved in suitable ILs, as described elsewhere^{E-1} for concentration values of polymers in IL as low as 4 wt %.^{H,I} Thus, the formation of stable gel-like composites between the polymeric chains of the nanostructure corona and the surrounding IL it might turn difficult to remove the IL trapped inside the corona (and surrounding the core) due to the highly viscous characteristics of the formed PEtOx corona-IL composites (see the cartoon in Figure S1). Moreover, it is known that the polymer blocks in PEtOx-*b*-PNonOx copolymers are in the weak segregation regime as confirmed by the observation of a single T_g in the bulk state.^J As suggested before,^J the values of the interaction parameters between each poly(oxazoline) block and the IL could be rather close although different enough to allow the formation of nanostructures. This means that the poly(oxazoline) block of the corona of the investigated nanostructures may be highly compatible with IL BMI-CF₃SO₃, which may lead to an ineffective removal of the IL in the corona when performing the washing procedure with water. Hence, it is thought that upon washing the dispersions of these specific nanostructures with a co-solvent which dissolves the IL (water in this case) it was sufficient to remove the matrix of IL, but not enough to break apart the highly viscous PEtOx corona-IL composite formed, and therefore a considerable amount of IL remains trapped in the corona (and surrounding the core). This scenario is also a suitable explanation for the good contrast observed in the TEM micrograph displayed in Figure S1 (high electron density due to the presence of IL BMI-CF₃SO₃ trapped in the entire nanostructures) and for supporting the hypothesis that the round shapes observed correspond to the overall size of the nanostructures (corona and core). Nevertheless, the relatively large structures observed in Figure S1 may also suggest the presence of aggregates of several micelles, which could be formed by the use of the co-solvent (water) during the described washing procedure for the TEM measurements.

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