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Conformational preference of a porphyrin rotor in confined environments†

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The amount of twisted conformation of a porphyrin rotor, when confined within ionic liquid reverse micelles, increased as compared to the neat solvents within a set of 1-alkyl-3-methylimidazolium ionic liquids. A similar trend was noted within DMSO-containing reverse micelles, indicating that the confinement might be a major contributor in the control of the rotor's conformation.

Ionic liquids (ILs) have been touted as customizable materials because their physical properties can easily be manipulated *via* modification of cation and anion pairs.[1] Consequently, the physical properties of ILs could impact various processes, which has lead to the idea of ILs as "designer solvents".[2]

Conventionally, the designer solvent ability of ILs has been illustrated predominantly within the realm of synthetic organic chemistry, where ILs have functioned as milieu for a number of synthetically useful reactions.[2–4] Recently, this concept was also expanded to include the use of various imidazolium-based ILs in the control of the conformational bias as well as self-assembly of small molecules.[5–8] The structural and physical properties of ILs were found to be crucial in modulating the aforementioned processes. The paradigm of controlling chemical, physical and structural properties of small molecules simply by placing them in structurally similar (yet distinct in regards to various physical properties) solvents is an interesting and potentially useful phenomenon which could result in intriguing applications of ILs.

Arguably, an alternative approach might be the modulation of ILs' environment rather than the structure, for example, if the ILs were placed within a confined environment.[9–11] In particular, encapsulation of an IL and a small molecule within a reverse micelle (RM) might give a different distribution of the conformations of the small molecule from that which was present when that molecule was dissolved in the neat IL. Notably, Falcone and co-workers reported that the confinement of ILs within IL–RMs could modify the microstructure of IL as compared to that observed in the bulk.[12,13] Therefore, we set out to investigate the effect of confinement on the conformation of a molecular rotor.

For our studies we selected a conjugated zinc porphyrin dimer, **PD** (Fig. 1).[14,15] **PD** undergoes a rotation around the diyne moiety resulting in a collection of conformations, with the twisted and planar conformations as two extremes (Fig. 1).[15] These twisted and planar conformations exhibit distinct emission maxima at around 710 and 780 nm, respectively, which allows for the facile determination of the conformation of **PD** in a variety of different media. In single component molecular solvents and mixtures of molecular solvents the conformational

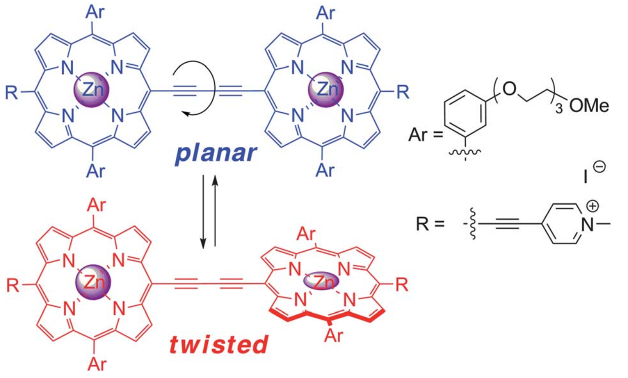

Fig. 1 Structure and conformational extremes of PD.

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preference of **PD** depends solely on the viscosity of the media, whereas the twisted conformation dominates in more viscous media such as glycerol or methanol–glycerol mixtures, for example, and the planar conformer exists in less viscous media such as neat methanol or ethanol.[7,15]

In the case of ILs on the other hand, the structure of IL was found to play an important role in the conformational bias of **PD**.[7] Specifically, in all ILs with a common cation, a similar conformation of **PD** was present, regardless of viscosity. Furthermore, an order of magnitude larger viscosity was required to promote a similar amount of the twisted conformation as compared to that found in the molecular solvents. This illustrated that the solute–solvent interactions of ILs with **PD** could control the conformation of **PD**, rather than the viscosity.[7]

In order to evaluate the effect of confinement on the conformation of **PD**, we prepared IL–RMs (also known as IL-in-oil RMs, *i.e.*, IL/O RMs) based on a modified version of a reported approach.[16,17] For this purpose, we utilized common, readily available imidazolium-based IL, such as [C$_4$-mim]PF$_6$, [C$_4$-mim]NTf$_2$ and [C$_4$-mim]NO$_3$. The corresponding IL–RMs were prepared by using a blend of two surfactants, namely polyoxyethylene sorbitan monooleate (Tween-80) and sorbitan laurate (Span-20), in isopropyl myristate (IPM). Using a fixed weight ratio of the surfactants (3 : 2 – Span-20 : Tween-80) and a fixed weight fraction of the surfactant blend (20 wt%) in IPM, various sizes of each IL–RMs were prepared by the addition of the appropriate amount of ILs to the surfactant blend in IPM. Subsequently, the formation and the size of the IL–RMs was evaluated using dynamic light scattering, DLS (Fig. S1†). According to the swelling law of RMs,[12] the incorporation of the ILs into the micelles can be confirmed using DLS if the size of the RMs increases linearly as the amount of ILs (or ratio of IL over surfactant blend, *i.e.*, R in Fig. S1†) increases. Interestingly, although the [C$_4$-mim]X ILs (where X = NO$_3$, PF$_6$ and NTf$_2$) had differing solubility in the surfactant blend–IPM solution, no drastic variation in the IL–RMs sizes were observed (Fig. S1†). Furthermore, we prepared IL–RMs with **PD** incorporated within the IL domain of the IL–RMs. It appeared that **PD** did not have a significant effect on the size of IL–RMs formed, as was indicated by similar DLS intensities for the **PD**-containing and **PD**-free IL–RMs (Fig. S1†).

With the suitable procedure for IL–RMs preparation at hand, we initially investigated the conformation of **PD** in [C$_4$-mim]PF$_6$-containing IL–RMs and compared it to neat [C$_4$-mim]PF$_6$, where **PD** was shown to exist largely in the planar conformation.[7] In PF$_6$-containing IL–RMs, although **PD** predominately adopted the planar conformation as indicated by the emission around 780 nm, the amount of the twisted conformation of **PD** was notably increased as compared to that observed in the neat [C$_4$-mim]PF$_6$ (Fig. 2A; for absorption spectra see Fig. S2†). In addition, a slight blue shift of the emission wavelength was also detected. Furthermore, we found that the amount of the IL and consequently concentration of **PD** (from 0.02 to 0.10 μM), as well as the amount of DMSO (up to 0.01% v/v) did not have an effect, as the planar conformation was observed as the major species no matter the size of the micelle, or concentration of **PD**.

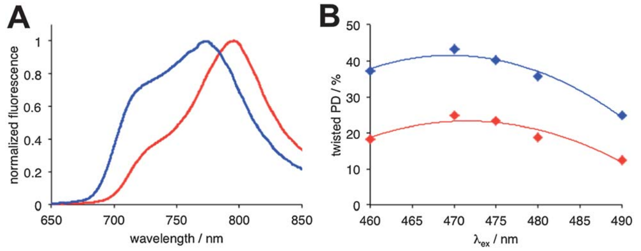

Fig. 2 Fluorescence spectra, where λ_{ex} = 475 nm (A) and the amount of the twisted conformation (B, the lines were added to guide the eye) of **PD** in neat [C$_4$-mim]PF$_6$ (red line and symbol) and in [C$_4$-mim]PF$_6$–RM (blue line and symbol). Conditions: [PD] = 0.10 μM, all mixtures contained 0.010% of DMSO (v/v).

It was previously shown that excitation of porphyrin rotors at different wavelengths (λ_{ex}), around the Soret absorption maximum, could elucidate the effect of the media on the distribution of their conformers.[18] Specifically, if the planar/twisted ratio was altered upon different λ_{ex}, then both conformers were present in a given media. On the contrary, if the ratio remained unchanged with varying λ_{ex}, then the existence of a single conformation was assumed.[18] Therefore, it could also be argued that if the ratio in IL–RMs is distinct from that found in neat ILs, the environment provided by the IL–RMs and neat ILs is also distinct. Accordingly, here we investigated the conformation of **PD** as a function of λ_{ex} in both neat [C$_4$-mim]PF$_6$ and [C$_4$-mim]PF$_6$–RM (Fig. 2B and S3†). In both neat ILs and IL–RMs, the ratio of **PD**'s conformations changed as a function of λ_{ex}, indicating that multiple conformations were present in both environments. However, the numerical values of the ratios in the two media were different, indicating that the natures of the IL-based media were distinct. Irrespective of the λ_{ex}, the amount of the twisted **PD** in IL–RM was always higher than that in the neat IL (Fig. 2B).

Next, in order to evaluate the effect of the anion (and, as such, the nature of the IL) on the conformation of **PD** in IL–RMs, we examined the fluorescence spectra of **PD** in IL–RMs, which contained [C$_4$-mim]NTf$_2$ and [C$_4$-mim]NO$_3$ ILs and compared them to those observed in neat ILs. In [C$_4$-mim]NTf$_2$–RM and neat [C$_4$-mim]NTf$_2$ (Fig. S4†), the difference between the amount of the different conformations of **PD** was somewhat similar to that observed for [C$_4$-mim]PF$_6$-containing system (Fig. 2), as an appreciable difference between the neat IL and IL–RM was evident (Fig. S4†). This similarity might be attributed to similar physical and/or structural properties of these two ILs.

On the contrary, in the case of the [C$_4$-mim]NO$_3$ IL, which is known to be distinct from both [C$_4$-mim]PF$_6$ and [C$_4$-mim]NTf$_2$ ILs (in regard to hydrophobicity, hygroscopicity, hydrogen bonding ability, *etc.*), the amount of the twisted **PD** in the neat IL was found to be somewhat similar to the amount observed when **PD** was placed in the IL–RM (Fig. S5†). However, the increase of the twisted conformation upon confinement within the RM was still observed over the range of the λ_{ex} (Fig. S5†).

Recently, it was shown that decreasing the length of the alkyl chain on the imidazolium cation, led to a decreased amount of the twisted conformation of **PD**.[7] If the confinement of an IL within RMs increases the twisted conformation, this change would be more prominent in those ILs in which **PD** exhibits the smallest amount of the twisted conformation. To probe the aforementioned hypothesis, we investigated the conformation of **PD** in [C_2-mim]BF_4 and [C_2-mim]NTf_2 ILs, as well as in their respective RMs. Similar to the [C_4-mim]-based ILs (Fig. S1†), a linear correlation between the diameter of the IL–RMs and the amount of ILs was observed for the [C_2-mim]-containing IL–RMs (Fig. S6†). In both of these systems (Fig. S7 and S8†), we found that the amount of the twisted conformation of **PD** increased from below 20% in neat ILs to slightly above 40% in the IL–RMs, thus confirming the aforementioned assumption that the amount of twisted conformation increases within IL–RMs.

Because the conformation of **PD** followed the same trend in all IL–RMs, regardless of the specific structure of the ILs, we hypothesized that the confinement itself could be responsible for the observed effect. As such, this phenomenon should exist regardless of the nature of the media *i.e.*, molecular organic solvent or IL. Therefore, we searched for a molecular organic solvent that promoted the planar conformation of **PD** in the bulk solvent, and was able to form RMs within the IPM–surfactant solution. DMSO was found to be a suitable solvent. It should be pointed out that unlike in neat ILs, **PD** in neat IPM was found to be non-fluorescent. Furthermore, when the DMSO stock solution of **PD** was diluted with other molecular solvents including EtOH, MeOH, EtOAc, DMF, $CHCl_3$, MeCN and acetone, and subsequently added to IPM as the media, no emission of **PD** was observed. All of the aforementioned solvents, except DMSO were found to be miscible with IPM. Therefore, the conformation of **PD** within DMSO–RMs was investigated. Similar to IL–RMs, the formation of DMSO–RMs was confirmed by the linear increase of the size of the RMs as a function of the amount of DMSO, *i.e.*, the *R* value (Fig. S9†).

We found that in all sizes of the DMSO–RMs, **PD** existed in nearly 45% of the twisted conformation (reminiscent of the behavior seen in IL–RMs), as opposed to neat DMSO where the twisted conformation of **PD** was around 15% (Fig. 3A and S10†). In addition, the amount of twisted conformation of **PD** experienced little variation as a function of λ_{ex} in neat DMSO, while in DMSO–RMs a trend similar to those observed in IL–RMs was observed (Fig. 3B). Thus, these results supported the hypothesis that the confinement might be a major factor in the control of **PD**'s conformation.

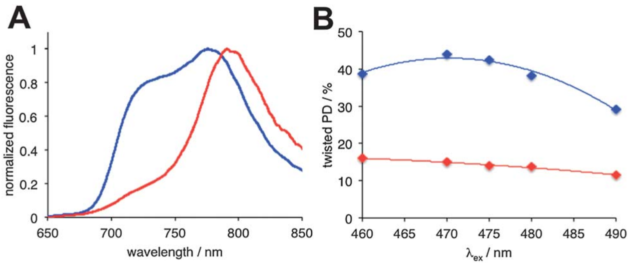

Fig. 3 Fluorescence spectra, where $\lambda_{ex} = 475$ nm (A) and the amount of the twisted conformation (B, the lines were added to guide the eye) of **PD** in neat DMSO (red line and symbol) and in DMSO–RM (blue line and symbol). Conditions: [**PD**] = 0.15 μM, all DMSO–RMs mixtures contained 1.5% of DMSO (v/v).

Conclusions

We have demonstrated that confining **PD** within RMs could play a pronounced role on the conformational preference of **PD**. Specifically, in RMs the amount of twisted conformation of **PD** was found to increase to *ca.* 40–45% as compared to that found in the neat solvents, *i.e.*, 15–25%, regardless of the nature (molecular or ionic) of the media. Thus, encapsulation of **PD** appeared to represent an alternative method to alter the conformational preference of this molecule. These results also suggested that the effect of confinement could override some specific solute–solvent interactions, which were shown to be important in control the conformation of **PD** in neat ILs.[7]

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