

Pyridinium Ionic Liquids as Charge Transfer Complexes

Beatrise Silava,^{a*} Eduards Baķis^a

^aDepartment of Chemistry, Faculty of Medicine and Life Sciences, University of Latvia, Jelgavas I, Riga LV-1004, Latvia

*E-mail: silavabeatrise@gmail.com

A promising alternative to conventional thermal activation in chemical reactions is the use of light energy. While photocatalysis typically relies on rare earth metal complexes, intrinsically photocatalytic solvents remain largely unexplored.

In this study, we investigated a new class of room-temperature ionic liquids (ILs) that are photoactive under UV-Vis irradiation, offering metal- and halogen-free fluids rich in ion radicals. This photoactivity is attributed to ion-pair charge transfer (CT) complex formation between various substituted pyridinium cations (CT acceptors) and the tricyanomethanide anion, [TCM]⁻ (CT donor) (figure 1).

The nature and energetics of ion pairing were studied in molecular solvents and in reference ILs containing the [NTf₂]⁻ anion, using UV-Vis spectroscopy and cyclic voltammetry. UV-Vis analysis revealed a distinct absorption band not observed in either [RPy][NTf₂] or K[TCM], confirming CT complex formation. Cyclic voltammetry showed that incorporating electron-withdrawing groups into the pyridinium ring shifts the reduction potentials to more positive values compared to unsubstituted analogues, demonstrating that the CT energy can be tuned.

These findings highlight the potential of [RPy][TCM] ILs as functional materials for photochemical applications, potentially providing a sustainable, metal- and halogen-free platform for light-driven chemical transformations. An ongoing work in our lab currently focuses on assessing the novel IL class in photocatalytic transformations for synthesis.

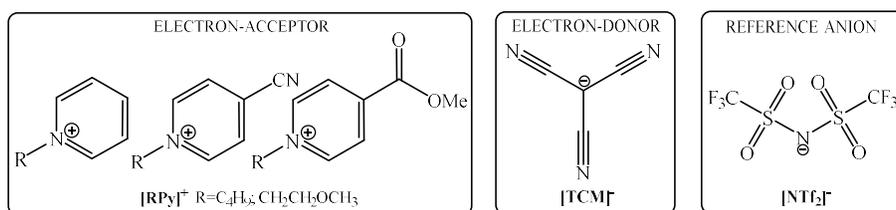


Figure 1. Ionic liquid ion structures studied in this work

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Beatrise Silava

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