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Design and Synthesis of Photoactive Ionic Liquids

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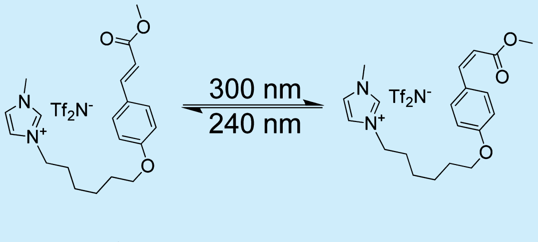
Ⓢ *Supporting Information*

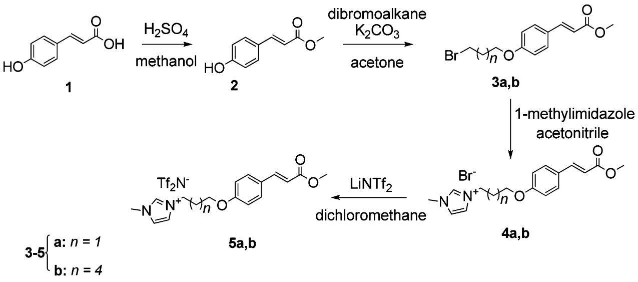
ABSTRACT: Two ionic liquids with photoisomerizable *p*-hydroxycinnamic acid moieties were synthesized and characterized by X-ray crystallography and DSC, and their photochemistry was studied in solution and neat conditions. Irradiation at absorption maxima led to *trans*–*cis* photoisomerization and resulted in significant reduction of melting temperatures of the ionic liquids. X-ray structures of both compounds show an intricate network of supramolecular interactions before irradiation. Physical and chemical transformations are completely reversible upon irradiation at lower wavelengths of ionic liquid solutions in acetonitrile.



Research in ionic liquids (ILs) is one of the most rapidly growing fields in recent years, focusing on the ultimate aim of large-scale industrial applications. Because of their unique physicochemical properties such as negligibly low vapor pressure at ambient temperatures, high ionic conductivity, and high thermal stability at elevated temperatures, ILs have attracted considerable technological and scientific interest in the past decade.[1] By varying the length of the alkane chains of the cationic core and the type or size of the anion, the physical properties of ILs can be tailored to meet the requirements of specific applications to create an almost infinite set of organic salts.[2−4] One of the main interests in ILs, in particular those that are liquid at room temperature (RTILs), arises from their applicability as an alternative to organic volatile solvents as reaction and extraction media,[5] where properties such as viscosity and liquid range play an important role.[6] Herein, we report the synthesis of novel ionic liquids whose melting points are reversibly tunable with light, leading to the formation of RTIL after irradiation of a solid salt. Photoresponsive ionic liquids (PRILs) have attracted considerable attention in the past decade due to attractive features such as photoresponsive magnetic moments or ionic conductivity and structure dependent photochromism.[7] Instead of relying on the photochemistry of diarylethene or azobenzene derivatives, which are usually expensive and difficult to prepare,[7c−e] the PRILs reported herein are based on cinnamic acid (CA) derivatives. CA is a naturally occurring and readily available photosensitive moiety, with well-characterized photochemistry[8,9] that has been applied extensively in photoresponsive systems.[10] In particular, photosensitive ionic liquids bearing CA have been prepared and have been shown to undergo photochemical *trans*-to-*cis* isomerization.[11] However, this reaction was used with the aim of separating both isomers and was not characterized in terms of quantum yields or reversibility. We report the first account of a photoresponsive ionic liquid bearing a natural photoresponsive moiety that exhibits reversible photochemistry that allows changes in their physical properties with light stimuli.

The syntheses of the compounds reported through this work are summarized in Scheme 1. The esterification of *p*-coumaric acid, **1**, is readily achieved through acid catalysis with H_2SO_4 in methanol. Alkylation of the phenol moiety is accomplished through nucleophilic substitution assisted with potassium carbonate in dry acetonitrile. The corresponding product, **3**, undergoes another nucleophilic substitution in the presence of *N*-methylimidazole to yield the imidazolium bromides **4a** and **4b**. Melting points of these ionic species were high (142 and 153 °C, respectively), and thus, anion metathesis with lithium bis(trifluoromethylsulfonyl)amide (Tf_2N^-) was performed to lower the melting point of the organic salts and yield ionic liquids **5a** and **5b**, with melting points at ca. 83 and 53 °C, respectively.

Scheme 1. Synthetic Pathway for the Preparation of Cinnamate Ionic Liquids 5a and 5b



Compounds **5a** and **5b** were dissolved in a mixture of $CHCl_3$ and MeOH 1:1, and the solution was allowed to be in contact

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with a slow diffusion of Et_2O leading to the formation of colorless single crystals with high quality for X-ray diffraction analysis which confirmed the formation of the two desired ILs (Figure 1). The crystal structures of the two compounds were determined in the triclinic space group *P*-1 with both asymmetric units revealing only one respective organic cation and one Tf_2N^- anion (detailed information on the crystallographic data collection and structure refinement are provided in the Supporting Information). The organic cation in compound **5a** reveals considerable planarity with the phenyl and the imidazolium rings practically in the same plane (the dihedral angle between the average planes of these two- aromatic groups is ca. 3.563°), while the structural arrangement of the organic cation in **5b** is significantly distinct, showing the imidazolium ring almost perpendicular to the phenyl group (the dihedral angle between the planes is ca. 79.341°). This structural difference is certainly related with the size of the alkylic chain between the cinnamate moieties and the imidazolium groups, as well as with the numerous C−H···X (X = F, N or O) intermolecular interactions involving adjacent organic cations and Tf_2N^- anions.

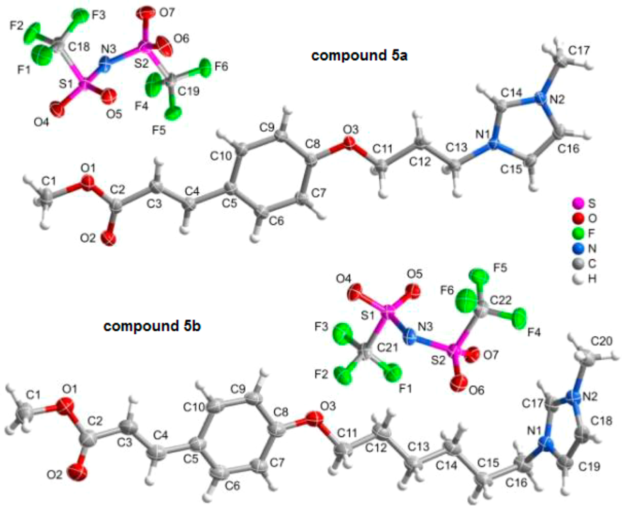

Figure 1. Crystal structures of the compounds **5a** and **5b**, showing the label scheme for all non-H atoms which are represented as thermal ellipsoids drawn at the 50% probability level, while H atoms are shown as small spheres with arbitrary radius.

In fact, the crystal packing arrangement in both **5a** and **5b** is strongly influenced by an extensive network of C−H···O weak hydrogen bonds involving neighboring organic cations, as well as C−H···F, C−H···N, and C−H···O between the organic moieties and the inorganic Tf_2N^- anions (see Figure S15 in the Supporting Information). In compound **5a**, the adjacent organic cations interact via three C−H···O bonds, while the inorganic anions establish various C−H···O and C−H···N weak hydrogen bond interactions with contiguous organic cations, leading to a 3D supramolecular structure (Supporting Information, Figure S15b). The same type of interactions are observed in the crystal packing of **5b**, ultimately leading to a 3D supramolecular network (Supporting Information, Figure S15c). In principle, irradiation of these ionic liquids should induce changes in the molecular structure, by isomerization and/or dimerization of the cinnamate moieties, and result in the disruption of the described intricate network of intermolecular interactions, eventually leading to observable changes in physical properties of **5a** and **5b**.

The photochemical behavior of ionic species **5a** and **5b** was initially investigated in acetonitrile. Both compounds underwent photochemical reactions when irradiated at their absorption maxima (Figure 2a). The decrease in absorbance around 300 nm and a slight increase in absorbance at lower wavelengths are consistent with the expected photoreactivity of cinnamic acid derivatives, i.e., photoisomerization and/or photodimerization, leading to species with blue-shifted maxima. In order to investigate the mechanism of the photochemical reaction, quantum yields (Φ_R) were calculated for a wide range of concentrations, from 10^{-5} to 10^{-2} M in acetonitrile and are summarized in Table 1. For both **5a** and **5b**, Φ_R values did not vary within this concentration range. This result led to the conclusion that an intramolecular reaction occurs upon irradiation, since the reaction rate does not depend on the concentration of the ionic liquid. Furthermore, the existence of an isosbestic point at 265 nm indicates that no secondary reactions occur during irradiation.[12] To corroborate these results, ^1H and ^{13}C NMR spectra were obtained for the irradiated solutions of both ionic liquids, and it was evidenced that photostationary states were composed only by both *trans*

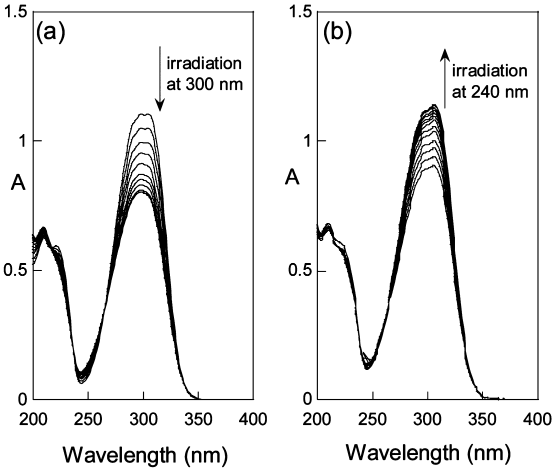

Figure 2. Spectral modifications of 5.4 × 10^{-5} M **5b** in acetonitrile upon irradiation at 300 nm (a) and 240 nm (b). Under the used experimental setup, the PSS was reached after 10 min irradiation at 300 nm, while the recovery upon irradiation at 240 nm required ca. 600 min.

Table 1. Absorption Maxima (λ_{max}), Photochemical Quantum Yields (Φ_R), and Cis Isomer Fraction before Irradiation and at the Photostationary State (PSS) of Ionic Liquids 5a and 5b in Acetonitrile

compd	λ_{max} (nm)	concn (M)	Φ_R	initial *cis* fraction	PSS *cis* fraction
5a	304	10^{-2}	0.12	0.0	0.47
		10^{-3}	0.11		
		10^{-4}	0.11		
		10^{-5}	0.12		
5b	304	10^{-2}	0.11	0.0	0.48
		10^{-3}	0.10		
		10^{-4}	0.12		
		10^{-5}	0.11		

and *cis* isomers in similar proportions (see details in the Supporting Information, Figures S22−S25). Therefore, the occurrence of photodimerization of cinnamate moieties was excluded for this concentration range, in accordance with previously described results for cinnamate ILs.[11] Moreover, the presence of decarboxylation products (arylethenes) was not detected. Further conversion of *trans*-**5** into *cis*-**5** was not possible due to the similar absorbance of both isomers at the excitation wavelength.[11,13]

The reversibility of the system was evaluated both thermally and photochemically, followed by UV−vis and ^{1}H NMR spectroscopy. Irradiated solutions were allowed to stand overnight at room temperature and thermal recovery was not detected, as expected for room temperatures.[14] In addition, neat samples at the photostationary state were kept at 120 °C for 8 h without giving rise to thermal recovery. On the other hand, both ionic liquids exhibited photochemical reversibility by irradiation at 240 nm. The spectral modifications observed by UV−vis show full recovery of the initial spectrum, Figure 2b. The degree of reversibility from isomer mixture to pure *trans*-**5** was further corroborated by NMR data (see the Supporting Information, Figures S26 and S27). Full conversion to the *trans*-isomer was achieved after long irradiation times due to the low absorption at the selected wavelength and lower *cis*-to-*trans* isomerization quantum yield (0.015).

The melting point (T_m) and enthalpies of melting (ΔH_m) of the ionic liquids were determined by differential scanning calorimetry (DSC). The obtained curves are depicted in Figure 3 and the corresponding values are summarized in Table 2.

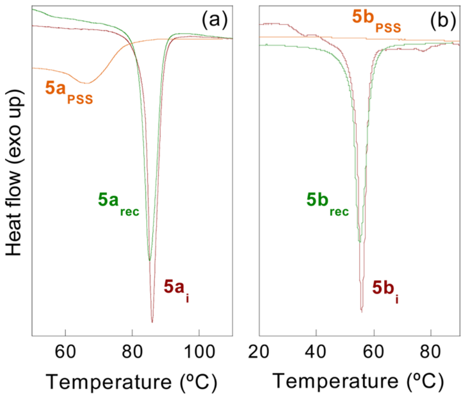

Figure 3. DSC curves of ionic liquids **5a** and **5b** before irradiation ($_i$), at the PSS ($_{PSS}$), and after recovery ($_{rec}$).

Table 2. Melting (T_m) and Peak (T_p) Temperatures and Melting Enthalpies (ΔH_m) of ILs 5a and 5b before Irradiation at 300 nm ($_i$), after the PSS Has Been Reached ($_{PSS}$) and after Recovery upon Irradiation at 240 nm ($_{rec}$)

	5a			5b		
compd	$5a_i$	$5a_{PSS}$	$5a_{rec}$	$5b_i$	$5b_{PSS}$	$5b_{rec}$
T_m (°C)	83.9	54.9	82.2	53.4		51.8
T_p (°C)	85.8	66.1	85.4	55.8	n.a.[a]	55.1
ΔH_m (J g^{-1})	67.1	20.9	63.3	62.3		62.2

[a] T_g at −42.8 °C.

Both **5a** and **5b** showed significantly lower melting points (onset temperatures) and ΔH_m after irradiation (photostationary state). While the pure *trans*-**5a** (**5a**$_i$) isomer had an initial melting point of 83 °C, its photostationary state (**5a**$_{PSS}$) composed by both *cis* and *trans* isomers melted at 55 °C. Moreover, its lower enthalpy of melting and larger difference between onset (T_m) and peak (T_p) temperatures indicates that the structural order is reduced after irradiation, due to the presence of both isomers.[15] For ionic liquid **5b**, the changes in physical properties were even more significant, Table 2. These results can be explained by the different intermolecular interactions established between the photoresponsive moieties in both ionic liquids. Whereas the proximity to the ionic domain in **5a** gives rise to interactions between cinnamate and the cationic and anionic cores (Supporting Information, Figure S15b), in **5b** these interactions are only established between cinnamate moieties (Supporting Information, Figure S15c). Upon isomerization, it is expected that loss of planarity in the photoresponsive core leads to the disruption of interactions between cinnamate moieties, while interactions with the ionic domain can still be established.

Upon irradiation at 240 nm to achieve complete recovery of *trans* isomers (**5a**,**b**$_{rec}$), both T_m and ΔH_m were measured by DSC. The values obtained are very close to those of nonirradiated samples (**5a**,**b**), showing that chemical and physical transformations are reversibly adjustable. After characterization of the photochemical behavior of ionic liquids **5a** and **5b** in solution, their photochemistry and resulting physical properties modifications were investigated in neat conditions. Both compounds were irradiated at 300 nm at their melting temperature as thin films, and the photochemical transformations were followed by ^{1}H NMR spectroscopy. NMR data show that, although **5a** and **5b** also undergo *trans*-to-*cis* isomerization upon irradiation under these conditions, other photochemical reactions take place with significant quantum yields, as indicated by the presence of several proton peaks with high chemical shifts (see the Supporting Information, Figure S28).

Photostationary states were achieved after 1 h of irradiation and were composed of a mixture of *trans*-**5** (ca. 45%), *cis*-**5** (ca. 30%), and other new compounds (ca. 25%). Although the complexity of the obtained NMR spectra complicaes the identification of the new species, it is expected that photo-oxidative processes occurring in the cinnamate moieties may give rise to different imidazolium salts. To test this hypothesis, ionic liquids **5a** and **5b** were melted, deaerated in vacuo, and irradiated under inert atmosphere.

NMR data show that, under these conditions, the extension of the photochemical byproducts is significantly reduced (<3%) (see the Supporting Information, Figure S29, for details). Since these experiments had to be carried out in closed quartz tubes to achieve inert atmosphere, ionic liquid samples had a low surface-to-volume ratio which in turn led to heterogeneous mixtures of isomers during irradiation.

Therefore, photochemical quantum yields could not be determined, and photostationary states were not achieved. However, melting points were still lowered after partial *trans* to *cis* isomerization of compounds **5a** and **5b** (for details, see the Supporting Information, Table S2). Moreover, it appears that melting temperature depression (ΔT_m) is directly proportional to the fraction of *cis*-**5** in the irradiated sample (Figure 4) and extrapolates to the values of irradiated solution samples with equal fractions of both isomers. These results suggest that irradiation of thin films of **5a** and **5b** under inert atmosphere would yield ΔT_m values similar to those obtained for irradiated solutions, if the same isomerization rate was achieved.

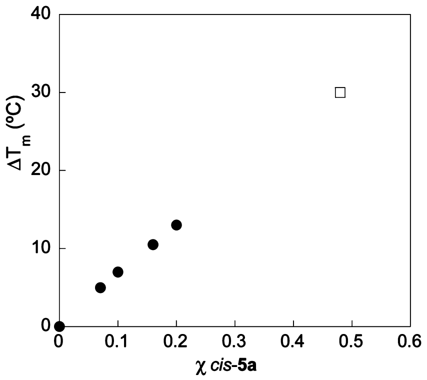

Figure 4. Isomer fraction dependency of melting temperature depression of irradiated neat samples (black dots) and acetonitrile solution (hollow square) of **5a**.

In conclusion, a new class of photoresponsive ionic liquids based on *trans*−*cis* isomerization of cinnamic acid derivatives was obtained through rational design. Physical properties, such as the melting point, of these compounds are addressable with light stimuli, which could be related to changes in intermolecular interactions in ionic clusters. In addition, these changes are reversible upon irradiation in solution. This behavior can be further explored for the tuning of properties that are governed by intermolecular interactions, such as viscosity or glass transition temperatures, to develop new photoresponsive RTILs, expanding their technological applicability as smart materials in fields ranging from microfluidics to drug delivery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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