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Nafion as an efficient reaction medium for diastereoselective photochemical reactions

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This Letter is dedicated to Professor V. Ramamurthy on the occasion of his 60th birthday

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Abstract

The ability of alkali ion exchanged Nafion interior to enhance the influence of chiral auxiliaries in photochemical reactions was examined with three independent asymmetric photoreactions, namely, photoisomerization of *trans*,*trans*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives, electro-cyclization of 2-oxo-1,2-dihydropyridine-1-acetic acid derivatives and oxa di-π methane rearrangement of 1,2-dihydro-2,2′-dimethylnapthalenone derivatives. Chiral auxiliaries that lead to 1:1 mixture of diastereomers in organic solvents yielded products in 5–21% diastereomeric excess when the photoreactions were carried out within the nanoclusters of alkali ion exchanged Nafion. The investigated systems also serve as probes to understand the mode of distribution of guest molecules within Nafion framework upon inclusion.

Asymmetric induction in photochemical reactions continues to be a challenging task due to the short lifetimes of excited states and low energy of activation for photoreactions.[1] Nonetheless, impressive asymmetric induction has been achieved when photochemical reactions are carried out in the crystalline state.[2] On the other hand, chiral induction in solution photochemistry has not received similar success. Recognizing the problem that not all molecules crystallize, several researchers, in particular Ramamurthy and Turro et al., explored the possibility of using various constrained media to achieve stereo selectivity in photochemical transformations.[3] Among the various hosts employed, faujasite zeolite yielded the most encouraging results.[4] Ramamurthy et al. have extensively investigated two different approaches involving zeolites, namely chiral inductor approach and chiral auxiliary approach.[3a] In the former, the guest and the chiral inductor are simultaneously included within zeolite and in the latter the chiral perturber is covalently appended to the guest prior to the inclusion within zeolites. Exploring these strategies, Ramamurthy et al. clearly demonstrated the utility of zeolite in obtaining moderate to high enantio- and diastereoselectivity in the products of photoreactions such as geometric isomerization, hydrogen abstraction and cyclization.[5] They obtained enantiomeric excess as high as 78% in the photocyclization of tropolone ethyl phenyl ether within sodium exchanged zeolite using chiral inductor approach.[6] Whereas their zeolite based chiral auxiliary strategy had routinely yielded diastereomeric excess >75% in systems such as photocyclization of tropolone derivatives and *N*-methyl pyridone derivatives, oxa di-π rearrangement of dihydrodimethylnapthalenone derivatives and cis–trans isomerization of diphenylcyclopropane carboxylic acid derivatives.[5b,7] Recently, Turro et al. demonstrated the value of dye-exchanged Y zeolite as an effective medium to control the stereo selectivity in the photo-oxygenation of chiral oxazolidinone-functionalized *Z*/*E* enecarbamates and had achieved enantioselectivity as high as 80%.[8]

In spite of noteworthy success achieved in asymmetric photoreaction within zeolites, the generality of zeolite

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based approach has been still under investigation. Also the dimensions of zeolites limit the size of the guest molecule that can be examined. These factors open up the room for exploring other constrained media that are suitable for inducing chirality in photochemical reactions. Using the previously established photoreactions within zeolite such as photo-Fries rearrangement of naphthyl esters, Norrish Type I reaction of 1-phenyl-3-*p*-tolyl-propan-2-one, Norrish Type I and Type II reactions of benzoin alkyl ethers and photodimerization of acenaphthylene as models,[9] we had recently demonstrated that the cations and confined interior provided by Nafion could be utilized to carry out photoreaction to yield selective products.[10] Also it was clearly shown in the report that the included guest molecules were in the close proximity to the cations of Nafion and the reactive excited state of the included guest could be modified by selectively choosing the counter cations of Nafion interior. Encouraged by these results, we envisioned that the cationic environment of Nafion could be explored to induce chirality during photochemical transformations similar to that of zeolites. Besides, Nafion based strategy has the following advantages: (a) the relatively larger size of Nafion ionic cluster compared to zeolite super cage permit us to include bigger molecules of photochemical interest which cannot be included within zeolites, (c) our previous experiments clearly indicated that there was no latent thermal reaction induced by Nafion interior and yielded high mass balance for photoreactions,[10] (d) Nafion is optically transparent to allow us to achieve high conversion.

In this context, we have examined the applicability of our strategy with three independent photochemical reactions, namely, photo-isomerization of $2\beta,3\beta$-diphenylcylopropane-1α-carboxylic acid derivatives (**1a**,**b**), oxa di-π rearrangement of 1,2-dihydro-2,2′-dimethylnapthalenone derivatives (**3a**,**b**) and electro-cyclization of 2-oxo-1,2-dihydropyridine-1-acetic acid derivatives (**5a**,**b**). The choice of our strategy, the photochemical systems and the chiral auxiliaries have been influenced by the following factors: (a) Chiral auxiliary approach has been the most successful one among the various zeolite based approaches.[7] (b) The photochemistry of **1a**–**b**, **3a**–**b** and **5a**–**b** were well established in solution phase.[11–13] (c) Upon irradiation within zeolite, the chosen substrates yielded products with high diastereoselectivity (50–80%) compared to their solution photochemistry (0–4%) and thereby provides an opportunity to test the effectiveness of Nafion host for asymmetric induction.[5b,14]

Nafion is a block copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octene sulfonic acid. When swollen in water or methanol, the sulfonic acid head groups are clustered together in solvent containing pockets of ca. 5 nm in diameter, which are interconnected through short channels (ca. 1 nm in diameter) within the fluorocarbon matrix (Fig. 1).[15] In our studies, Nafion beads in its alkali ion form were used. The protons of commercially available Nafion beads can be easily exchanged for alkali metal cations by treating H^+ Nafion with corresponding aqueous alkali metal hydroxide solutions. Solvent swollen Nafion can incorporate high concentrations of hydrocarbons within its ionic clusters,[16] and has been explored as a reaction medium in the recent past.[17] Previous photophysical studies within Nafion using probes such as pyrene, xanthone and benzophenone suggest that aromatic hydrocarbons when incorporated within Nafion matrix are located within the ionic cluster or at the interface between fluorocarbon backbone and ionic cluster.[18] A typical methodology for adsorbing the guests into Nafion interior includes stirring a known amount of Nafion beads (300 mg) in a methanolic solution of substrate (**1a**–**b**, **3a**–**b** and **5a**–**b**) of known concentration (12–15 mM). The solvent was removed under reduced pressure to obtain dry Nafion beads. The amount of loading is dictated by the concentration of methanolic solution of the substrates that are used to swell the Nafion beads. With the help of parameters available in the literature,[17e,19] an appropriate loading level (2.0–2.65 mg of the substrates/300 mg of Nafion) was chosen so that the average occupancy number (i.e., the number of guest molecules in the close proximity of each ionic cluster of Nafion) of the samples to be $\sim$1. The concentration of methanolic solution of the substrates required to get the chosen loading level was calculated from our previous experiments on the inclusion of probe molecules of similar size and the exact amount of the substrate incorporated was calculated from calibration studies.[20] Photolysis was carried out with dry samples following which the photoproducts were extracted with methanol–acetonitrile mixture. The diastereomeric products from **1a**,**b** and **3a**,**b** were analyzed in GC using SE 30 column and diastereomeric products from **5a**,**b** were analyzed in HPLC using chiral column AD-RH. The photoproducts are isolated and characterized by ^{1}H NMR and the spectral data are consistent with literature reports.[5b,11–14]

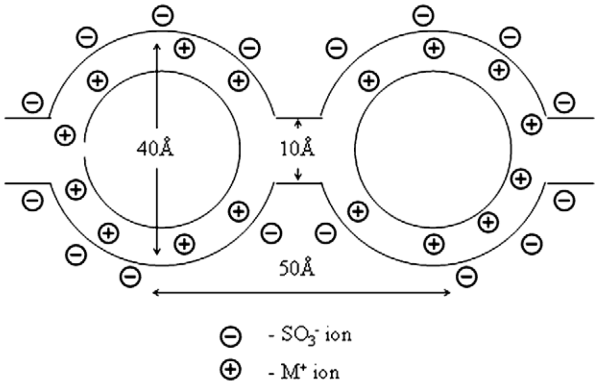
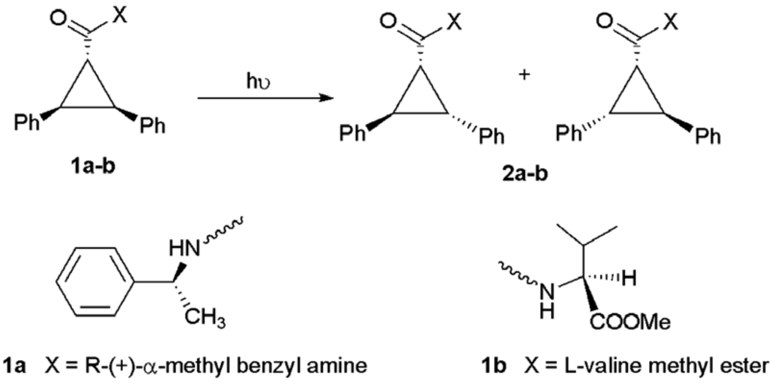


Fig. 1. Ionic cluster model of Nafion reported in the literature.[15]

The first reaction investigated was *trans*,*trans*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives **1a** and **1b**, in which the chiral auxiliaries *R*-(+)-α-methyl benzyl amine and L-valine methyl ester were, respectively, attached through amide linkage. Upon irradiation above 220 nm, **1a** and **1b** undergo photoisomerization to yield



Scheme 1. Photoisomerization of *trans*,*trans*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives.

Table 1
Diastereoselectivities obtained upon the photolysis of **1a** and **1b**[a]

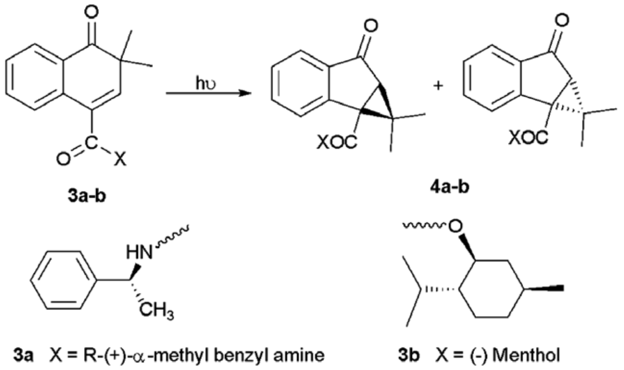
Reactant	Medium	Diastereomeric excess[b] (%)
1a	Acetonitrile	3 (A)
1a	Na^+ Nafion	5 (A)
1a	Li^+ Nafion	5 (A)
1b	Acetonitrile	0
1b	Na^+ Nafion	5 (B)
1b	Li^+ Nafion	5 (B)

[a] For details of structure, see Scheme 1.

[b] The first peak that elutes out of the GC column is assigned as A and the second as B.

diastereomeric trans isomers **2a** and **2b**, respectively (Scheme 1).[11] In isotropic solvents such as acetonitrile, **1a** and **1b** yielded the corresponding diastereomeric trans isomers with 0–3% diastereomeric excess. Whereas photoisomerization within Na^+ and Li^+ Nafion beads yielded the respective products with 5% diastereomeric excess as presented in Table 1.

The oxa di-π methane rearrangement of 2,2-dimethy-1,2-dihydronapthalenone-4-carboxylic acid derivatives **3a** and **3b** was then investigated. *R*-(+)-α-Methyl benzyl amine and (−) menthol were, respectively, used as chiral auxiliaries in **3a** and **3b**. Irradiation of **3a**,**b** at wavelength above 330 nm resulted in chiral products benzobicyclo[3.1.0]hexenone derivatives (**4a**,**b**) via oxa di-π methane rearrangement (Scheme 2).[12] Results upon the photolysis of **3a**,**b** in various media are summarized in Table 2. We observed a 14% diastereomeric excess in the case of **3a** and a 13% diastereomeric excess for **3b** from the photoreaction within Na^+ Nafion while the solution photochemistry gave the products with only 5% diastereomeric excess for both the chiral auxiliaries. Photolysis of **3a** and **3b** within Li^+ Nafion beads resulted in 8% diastereomeric excess.



Scheme 2. Oxa di-π methane rearrangement of 1,2-dihydro-2,2-dimethylnapthalenone derivatives.

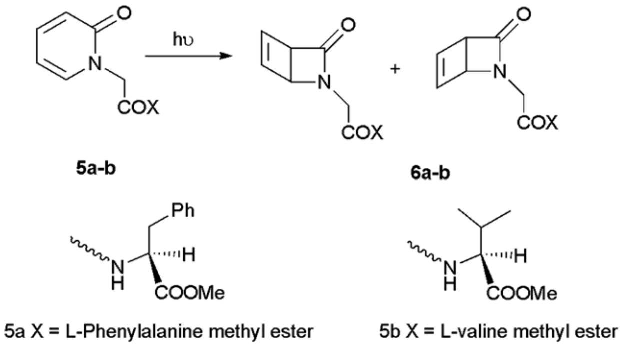
Table 2
Diastereoselectivities obtained upon the photolysis of **3a** and **3b**[a]

Reactant	Medium	Diastereomeric excess[b] (%)
3a	Acetonitrile	5 (B)
3a	Na^+ Nafion	14 (B)
3a	Li^+ Nafion	8 (B)
3b	Acetonitrile	5 (B)
3b	Na^+ Nafion	13 (B)
3b	Li^+ Nafion	8 (B)

[a] For details of structure, see Scheme 2.

[b] The first peak that elutes out of the GC column is assigned as A and the second as B.

The ability of Nafion matrix to effect asymmetric induction was tested with one more system, namely, electrocyclization of 2-oxo-1,2-dihydropyridine-1-acetic acid derivatives (**5a**,**b**) possessing chiral auxiliaries L-valine methyl ester and L-phenylalanine methyl ester. They undergo electrocyclization upon irradiation above 270 nm to yield diastereomeric bicyclic products **6a** and **6b** (Scheme 3).[5b] Results obtained from electrocyclization of **5a**,**b** in various media are summarized in Table 3. Irradiation of **5a** and **5b** within Na^+ Nafion yielded the bicyclic products **6a** and **6b** with 21% (Fig. 2) and 15% diastereomeric excesses respectively, whereas the solution photochemistry yielded only 0–4% diastereomeric excesses. Irradiation of the same within Li^+ Nafion resulted in the respective products **6a** and **6b** with 15% and 13% diastereomeric excess. As a part of control experiments, substrates **1a**–**b**, **3a**–**b** and **5a**–**b** were made to adsorb on the exterior fluorocarbon matrix of Na^+ Nafion beads and irradiated.[13] Photochemistry of the guest molecules (**1a**–**b**, **3a**–**b** and **5a**–**b**) adsorbed on the exterior fluorocarbon matrix of Nafion beads yielded the respective products with only 0–3% diastereomeric excess.[21]



Scheme 3. Photocyclization of pyridone-*N*-methyl carboxylic acid derivatives.

Table 3
Diastereoselectivities obtained upon the photolysis of **5a** and **5b**[a]

Reactant	Medium	Diastereomeric excess[b] (%)
5a	Acetonitrile	4 (A)
5a	Na^+ Nafion	21 (A)
5a	Li^+ Nafion	5 (A)
5b	Acetonitrile	0
5b	Na^+ Nafion	15 (B)
5b	Li^+ Nafion	13 (B)

[a] For details of structure, see Scheme 3.

[b] The first peak that elutes out of the GC column is assigned as A and the second as B.

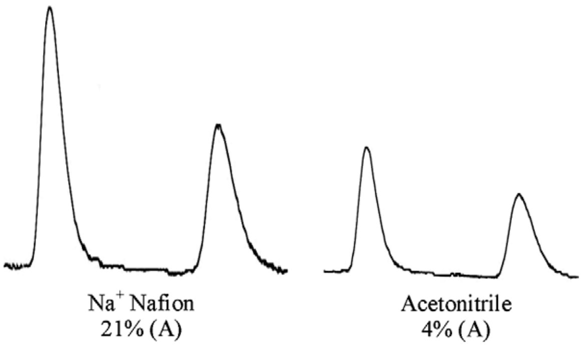


Fig. 2. HPLC trace showing diastereoselectivity obtained in photocyclization of 1-methyl carboxy-2-pyridone derivative **5a**.

Our preliminary experiments clearly suggest that the influence of chiral auxiliaries in asymmetric induction during a photochemical transformation is appreciably enhanced (5–21%) within Na^+ and Li^+ Nafion beads relative to its solution photochemistry. The comparison of the results that is obtained in isotropic media with that of Na^+ Nafion along with the control experiments illustrates the importance of the Nafion interior in achieving diastereoselectivity. As in zeolites,[22] it is presumed that the different conformational preference for the reactant molecule within the ionic clusters of Nafion, resulting from cation–substrate interaction, combined with the confinement provided by the Nafion interior is responsible for the asymmetric induction. Previous work on Nafion reported by us[10] and other research groups[18] clearly demonstrate the role of cations of Nafion in altering photophysical and photochemical properties of the incorporated organic molecules and our present results further highlight the value of counter cations of Nafion in manipulating the outcome of the excited state process of guest molecules. In all our investigated systems (**1a**–**b**, **3a**–**b** and **5a**–**b**), the diastereoselectivity did not vary with the conversion (15–90%). This emphasize the fact that the influence on the shape of remaining space exerted by products formation, at our chosen loading level (average occupancy number ~1), has no or minimal effect on dictating the diastereoselectivity of the products.

As evident from our results, the extent of chiral induction is different for different substrates as the percentage diastereoselectivity depends on the mode and efficiency of the cation–substrate interaction. Also we presume on the basis of our preliminary experiments that the magnitude of stereoselectivity depends on the distribution of the included guest molecules. The guest molecules that are in the close proximity to the cations yield products with high diastereoselectivity. The guest molecules that are trapped farther away from the cations lead to low selectivity. The observed diastereoselectivity in products is most likely the resultant of the asymmetric induction obtained from the guest molecules that are closer and farther to the cations of Nafion frame work. The general understanding based on our previous experiments,[10] present study and the literature[17] on Nafion photochemistry is that the distribution of the incorporated guest molecules within Nafion is dependent on their polarity. We believe that by carefully choosing the chiral auxiliary that could both act as chiral template and direct the guest molecules in the close proximity of cations of Nafion, the diastereoselectivity could be improved. However, further investigation along this line is needed to achieve more generality in Nafion based strategy. Also the hydration of cations by trace amount of moisture present even after drying under reduced pressure[19] most likely stands as another limitation for obtaining higher selectivity within Nafion. This speculation is supported, at least partially, by the low diastereoselectivity obtained within Li^+ Nafion (compared to Na^+ Nafion), where the cations are hydrated to a greater extent.[19] However, better understanding on the dependence of diastereoselectivity on the nature of the counter cations requires further studies on Nafion exchanged with various cations.

In conclusion, we have shown that alkali ion exchanged Nafion can be used as a photochemical reaction medium to achieve appreciable (5–21%) chiral induction. The selectivity is significant compared to their solution photochemistry but moderate at best when compared to that of zeolite based approach. Nevertheless, the information from our preliminary experiments will help to establish a concept and generate model for future studies. We envisage that the knowledge of chiral recognization within polymeric media is very important for its application in biomimics. Our future goals in the area of Nafion based chiral induction strategy are (1) to establish a 'general model' of Nafion based strategy for asymmetric induction in photochemical reaction by examining more photochemical systems with various structurally and electronically different chiral auxiliaries and by investigating the utility of Nafion exchanged with other cations such as K$^+$, Rb$^+$ and Cs$^+$ in chiral induction and (2) to modify the sulfonic acid groups of Nafion with chiral organic cations and investigate the utility of chirally modified Nafion in asymmetric photochemical reactions of achiral molecules and molecules with chiral auxiliary. On the synthetic point of view, the convenience of their handling, room for further modification, hope for reusability make Nafion as a promising reaction medium worth further investigation.

Acknowledgements

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20. The amount of substrates incorporated into Nafion beads was calculated by extracting the substrated loaded Nafion beads with acetonitrile–methanol mixture and analyzing using GC (Shimadzu 17A) with docosane as internal standard. Loading level (mg/300 mg of Nafion beads): **1a**—2.58 mg, **1b**—2.64 mg, **3a**—2.41 mg, **3b**—2.65 mg, **5a**—2.39 mg, **5b**—2.02 mg.
21. Substrates **1**, **3** and **5** were made to adsorb on the exterior fluorocarbon matrix of Na$^+$ Nafion by stirring the Nafion beads in the corresponding dichloromethane solution of the reactant followed by the removal of the solvent under reduced pressure. Dichloromethane did not swell the polymer and the reactant just got adsorbed on the exterior fluorocarbon matrix.
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