Supporting information

Acid-catalyzed Oligomerization via Activated Proton Transfer to Aromatic and Unsaturated Monomers in Nafion Membranes: A step forward in the in situ synthesis of Conjugated Composite Membranes

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Spectroscopy of protonated/hydrated and deprotonated/dehydrated Nafion membranes:



Figure S1. (a) FTIR and (b) UV-visible spectra of protonated/hydrated nafion (black) and spectra 2 deprotonated/ dehydrated nafion (red) membrane.

To perform the detailed IR and UV-visible investigation on this acidic nafion membrane. It is very important to know its Infrared as well electronic spectral differences in protonated (hydrated) and deprotonated (dehydrated) states. The Nafion membrane is prepared by a technique as mentioned in Experimental section. The as prepared Nafion membrane inserted in a gold envelope and put in quartz IR cell equipped with KBr windows outgas in high vacuum at 100°C and registered the IR spectra 1 in Figure S1 (a).

The broad adsorption band at 3000 cm⁻¹ is due to the nests of $-SO_3H$ groups interacting with intermolecular H-bonding represents compact chains of perflurocarbon [1]. In low frequency region observed the sharp bands at 1040 and

910 cm⁻¹ is due to v (S=O) and v (S-OH) stretching respectively which are significant bands of protonated Nafion (P-SO₃H) membrane this clarifies the protonated state of Nafion membrane [1],[2],[3]. By simple approach of dosing water on above Nafion polymer sample we registered the spectra 2 in Figure S1 the broad band at 3000 cm⁻¹ (spectra (a)) disappeared and a new broad band at 3500 cm⁻¹ and 1700 cm⁻¹ formed which is due to H₂O, H₃O⁺ species. Most importantly there is disappearance of the band at 1040 and 910 cm⁻¹ and appearance of the sharp band at 1060 cm⁻¹ of the SO₃⁻ species of Nafion [3].

Above IR spectral changes indicates clearly that as we go from hydrated (protonated) to dehydrate (deprotonated) Nafion membrane following reaction take place:

 $n^*P-SO_3H + nH_2O \leftrightarrow ^*P-SO_3^- + H_3O^+$; Where $^*P - Nafion (C_9HF_{17}O_5S)$

The UV-Visible spectra of Nafion (prepared on silicon wafer as mentioned above) outgas at 100° C for 30 min. show broad band at 277 nm/36000 cm⁻¹ in Figure s1 (b) (black spectrum 1). It gives us a distinguishing feature between protonated and deprotonated Nafion membrane as completely absent in Nafion after dosing H₂O deprotonated state in Figure S1(b) (red spectrum 2).

The UV-Visible absorption bands of Nafion membrane are difficult to interpret. Several studies [4],[5] have reported that Nafion membrane submitted to high temperature (100° C) exhibits structural changes described as shrinkage of clusters and polymeric reorientation also this indicates the lower thermal stability of Nafion membrane.

The band at 277 nm is associated with a carbonyl chromophore (the source of carbon is doubtful as we are carrying out reaction in vacuum). The Increase in the

intensity of the band at 277 nm with increasing temperature, is partially associated to radical species formed by the scission of the C-S bond of the Sulfonic acid group. When nafion is heated about 5% weight loss occurs the gases evolved are H_2O , SO_2 and CO_2 [6].

Table S1. FTIR and UV-visible Spectroscopic difference between protonated (H-Nafion) and deprotonated Nafion membrane. Where, $P = Nafion (C_9HF_{17}O_5S)$

Spectroscopic technique	P-SO3H : Protonated	P-SO3 ⁻ : Deprotonated
useu		
$FTIR (cm^{-1})$	910 v(S-OH) ; 1410	1060 v(SO ₃ ⁻)
	v(S=O)	
UV –Visible (cm ⁻¹)	36000 (unknown)	-
UV –Visible (cm ⁻¹)	v(S=O) 36000 (unknown)	-





Figure S2. Gas phase spectrum of Pyrrol (a), Thiophene (b), Furan (c) and Methylacetylene (d) [7] [Nist]

Table S2 The characteristic modes of vibration [NIST] database for Pyrrol,Thiophene, Furan and Methylacetylene [7].

Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment		
Ру	Pyrrol _(g)		Thiophene _(g)		
3410	v(N-H) strech	3098 and 3126	Aromatic v(C-H) streches		
1549, 1470,1428 and 1163	Ring streches	1256, 1083 and 1036	C-H deformation in plane		
3170-3130	Aromatic v(C-H) streches	683,712,867 and 898	C-H deformation out of plane		
1294.1076,1050 and 1029	C-H deformation in plane	1409,1360, 839,1507 and 872	Ring streches		
897,865,735 and 738	C-H deformation out of plane	608 and 751	In plane ring deformation		
1156	N-H deformation in plane	565 and 452	out of plane ring deformation		
611 N-H deformation out of plane		Methyl-acetylene (g)			
895 and 885	Deformation modes of ring	3334	v(≡C-H) bond strech		
612 and 618	Torsion modes of ring	3008	Asymmetric CH ₃ stretching		
Furan _(g)		2941-2881	Symmetric stretching v(CH ₃		
3089 and 3120	Aromatic v(C-H) streches	2142	v(C≡C) bond strech		
1264,1073 and 999	C-H deformation in plane	1452	Asymmetric CH ₃ deformation		
1490,1387,1189,725	Ring streches	931	V(C-C) strech		
1580 and 624	Ring deformation in plane	633	C-H bond bending		
763	C-H deformation out of plane	328	C-C-C bond bending		
872	Ring deformation out of plane		1		



Figure S3. IR and UV-visible spectra of Methylacetylene/Nafion system: (a) Total spectrum (3500-650 cm⁻¹), (b) magnification of the fingerprint region 1800-650 cm⁻¹.

The UV-visible spectra of Methylacetylene/Nafion system in Figure S3: Black Spectrum : H-Nafion degassed at 100°C K for 30 min; Grey spectra (spectrum 2 to 6 and i to vi) represents the effect of increasing contact time (about 2 minutes interval for each spectrum) after a dosage of Methylacetylene gas monomers on Nafion membrane at room temperature; red spectra (7 and vii) represents Methylacetylene/Nafion system after annealing in presence of excess of Methylacetylene gas phase at 100°C for 30 minutes. Blue Spectrum 8 and viii: after degassing Methylacetylene gas phase reactant. We also note that in the last spectra the presence of weak band intensity at about 526 and 666 nm suggests the formation (although very low concentrations) of polymeric species with higher nuclearity (tetramers and pentamers).



Scheme I





Scheme III



Figure S4. Illustration of the three main parts of the activated proton transfer reaction.

EXPERIMENTAL DETAILS

Materials:

A commercially available Nafion ion-exchange resin was used in these experiments to form the Nafion membrane and was supplied by Sigma Aldrich as a 20 wt.% solution in lower aliphatic alcohols/H₂O (34% water). Thin membrane films of Nafion polymers can be produced by depositing a layer of concentrated Nafion EW 1100 solution in an aliphatic alcohols/water mixture¹² (purchased from Aldrich Chemicals Co. Ltd.) and applied on a silica plate letting the solvents slowly evaporate at room temperature until a solid polymeric film (1-5 mg/cm²) is formed on the flat silica surface. The film was then gently removed and fixed to a gold rectangular sample holder with a central hole of about 5 mm diameter. The sample holder was then inserted into a quartz cell, equipped with KBr windows, allowing IR transmission experiments as well as thermal treatment under high vacuum. The cell was

permanently connected to a vacuum system and to a gas manifold allowing *In-situ* gas dosage on the sample placed on the spectrometer beam. The amount of dosed gas was quantified by measuring the pressure before and after each dose. The FTIR spectrometer was a Bruker 66 instrument with MCT detector with a spectral resolution of 2 cm⁻¹. Before adsorption of the unsaturated or heterocyclic molecules the polymer films were outgassed at 120°C under vacuum for 1 hour in order to remove water and other adsorbed impurities.

For the optical spectroscopy measurements (UV-Visible in transmittance mode using a Cary 5 spectrometer) the sample was deposited on a guartz slide letting the solvent evaporated at room temperature until it was solidified and the guartz slide (with the polymer film on it) was then inserted into the quartz cell described before. All other subsequent procedures were identical as in the case of the FTIR measurements. For all the investigated reaction products the spectroscopic measurements were performed using self-supporting Nafion films suitable for IR and UV-Vis transmission measurements. In all cases the Nafion membrane was placed in a cell allowing outgassing of the membrane at 100°C under vacuum and dosage of the studied molecule from the gas phase. The experiments were therefore performed in absence of water or oxygen contamination. After each dosage of the molecule under investigation, the oligomerization reaction was spectroscopically studied as a function of contact time with the hybridization material vapour (up to 24 hrs) and the temperature (up to 100°C) Thermal treatments of the Oligomer/Nafion systems were performed *in situ* in the presence of Pyrrole, Thiophene, Furan or Methyl-acetylene in the gas phase. (At corresponding vapour pressure of the particular molecules at room temperature).

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Density functional theory (DFT) calculations were performed using the Gaussian09 package¹³ on a B3LYP/6-311G(d,p) level. All structures were geometry optimized to the electronic ground state where after linear response DFT and time dependent (TD)

DFT was utilized for theoretical IR spectra and optical transitions, respectively.

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