Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

Low toxic environment friendly single component aqueous organic ionic conductors for high efficiency Photoelectrochemical Solar Cells

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Experimental

Materials and Reagents

All reactions were performed under an argon atmosphere and appropriate solvents were distilled from drying agents prior to use. The starting materials of OICs, methyl phenyl ketone (>98%), 2-pyridinecarboxaldehyde (99%), potassium hydroxide pellets (85%), hydroiodic acid (HI) (55-58%) and hydrobromic acid (HBr) (48%) were purchased from Sigma-Aldrich and Alfa-Aesar. The nano-crystalline TiO_2 semiconductor (<20 nm, 99.7%, anatase), lithium iodide (LiI), iodine (I_2), 3-methoxypropionitrile (MNP), Guanidiniumthiocyanate (GSCN), 4-tert butyl pyridine (TBP), ethyl cellulose (90.2%) and α-terpineol (90%) having high purity were purchased from Sigma-Aldrich chemicals. FTO substrates ($7\Omega/cm^2$) and hot melt tape (25μm) were purchased from Sigma-Aldrich. The organic solvent such as diethyl ether, acetonitrile, and ethanol were purchased from Merck. The metal-free carbazole organic sensitizer, SK3 was prepared as per our previous report.[1]

Fabrication of aqueous photovoltaic devices

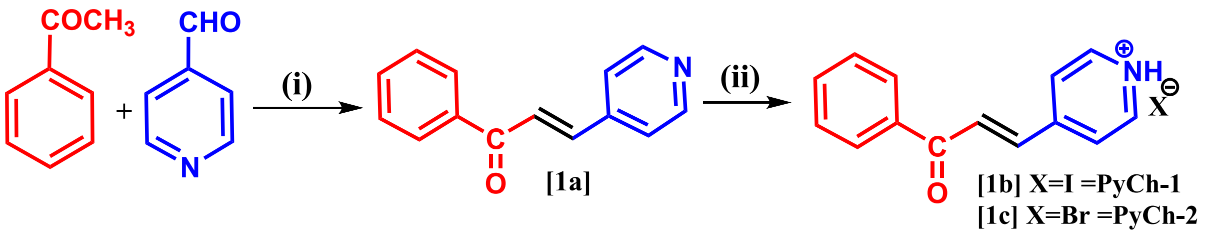
The preparation of TiO_2 photoelectrode was done as per our previously reported method.[2-3] To prepare the photoanode for DSSCs, FTO glass substrates were cleaned by sequential sonication in a detergent, DI water, and ethanol and were dried in a N_2 stream. After this treatment, were coated with a buffer layer of TiO_2 by spin coating (2000rpm, 60s) followed by annealing at 450˚C. Then TiO_2 film with a thickness of 12 μm was formed on this coated substrate by the doctor blade technique as follows. A thin film of the TiO_2 particles was deposited from the TiO_2 paste containing ethyl cellulose and α-terpineol. The electrodes were annealing in tubular furnace at 450 °C for 15 minutes and then soaked in the 30mM dye (metal free dye, SK3) solution. The dye soaking was carried out at room temperature for 24 hrs. Thereafter, the dye-adsorbed by TiO_2 electrodes were taken out and rinsed with dry ethanol. The rinsing process was repeated 2-3 times to wash out unbound dyes completely. Finally, the dye sensitized TiO_2 films were dried in air. Counter electrodes was fabricated by spin coating of 50mM H_2PtCl_6 solution in IPA on FTO substrate followed by sintering at 450˚C for 15 min. Dye sensitized photoanode and Pt-counter electrode were sealed together using hot melt sealing tape. AOICs electrolyte solution fills in between two electrode gap. The active area of the DSSC was set to 0.2 cm^2 and was maintained constant using the same mask.

Characterization

The OICs were synthesized by claisen-Schmidt condensation method according to the published journals.[4] ^1H and ^{13}C NMR spectra were recorded using a Bruker 400 MHz NMR instrument and residual signal of the solvent was taken in DMSO-d_6. The UV-vis absorption spectra experiments were done in UV-vis spectrophotometer (UV-160A). Thermogravimetric (TG) analysis was performed on a TGA system (TGA-Q500) at a heating rate of 5 ˚C min^{-1}. Cyclic Voltammetry (CV) was performed Autolab (Metrohm) instrument with three standard electrochemical cells. The Ag/AgCl electrode as the reference, carbon electrode as a working electrode and Pt wire for counter electrode. 0.1 M tetra-butyl ammonium hexaflurophosphate ($TBAPF_6$) for supporting electrolyte dissolved in acetonitrile solvent. Raman spectra were measured by using Horiba JobinYvon modular Raman spectrometer with a green laser (514nm, Stellar Pro Argon-ion laser). Theoretical calculation obtains by TD-DFT, using B3LYP, 6-31G basic set.

The photocurrent density-voltage (*J*-*V*) characteristics of the fabricated DSSCs were measured by using Keithley-2450 source meter controlled by a computer scan rate of 10 mVs^{-1}. A solar simulator (Newport Oriel) 500 W xenon lamp, connected with an AM 1.5 Globe filter to serve as the light source, give 100mW/cm^2 at the surface of the test cell to remove ultraviolet and infrared radiation. The External quantum efficiency (EQE) of the devices was recorded using a Zolix (SCS10-X150-DSSC), where a 250 W quartz tungsten halogen (QTH) lamp was used as the light source. While Electrochemical Impedance spectroscopy (EIS) measurements were carried out using Metrohm (Autolab FRA32) electrochemical analyser and data were analysed using Nova 1.11.1 software. EIS of the DSSC was measured by sweeping low amplitude AC signal (10mV) having a frequency ranging from 100 kHz to 0.1 Hz. During the measurement, cells were held in dark under the application of -0.65 V DC bias. Open circuit voltage decay (OCVD) was obtained by same Autolab instrument and calculated electron lifetime of devices. Tafel polarization curves were measured by sweeping potential from ±0.6V to the DSSC in dark and resulting data were fitted in Buttler-Volmer equation.

Synthesis of Organic Ionic Conductors



Scheme 1. Reaction scheme for organic ionic conductors. (Reaction condition; (i) KOH, ethanol, 25˚C, 24hr and (ii) THF, hydroiodic acid or hydrobromic acid, stirring for 24hr.

*Synthesis of pyridine chalcone [**1a**]:*

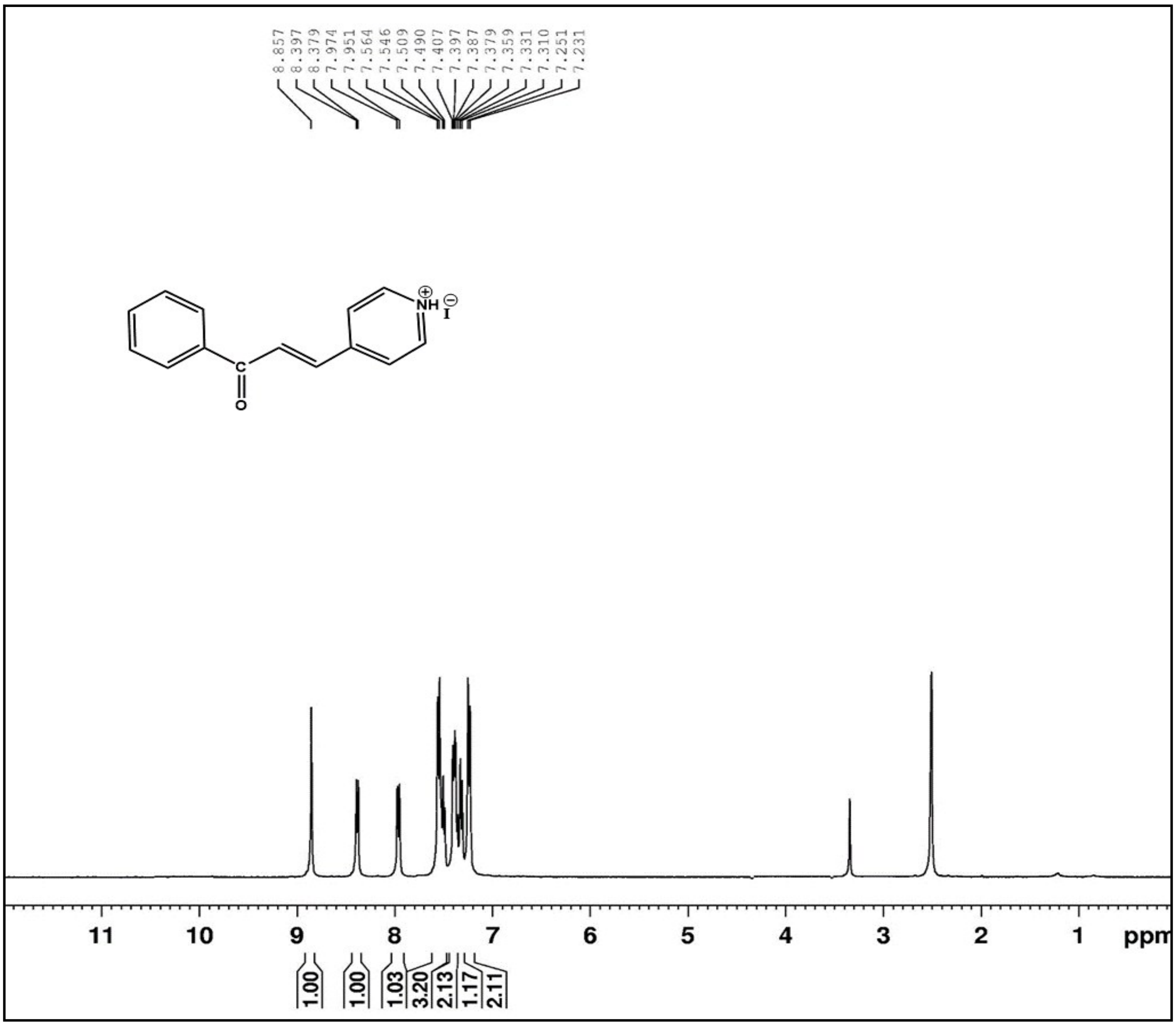
In round bottom flask, 1:1 mole of methyl phenyl ketone and 2-pyridinecarboxaldehyde were mixed in ethanol and the system was made basic using potassium hydroxide pellets. The reaction mixture was stirred at 25˚C for 24 hr and was monitored by TLC. At the end of the reaction, the entire reaction mass was poured into cold water and the final product was separated by adding diethyl ether to the aqueous phase. After purification by silica gel column chromatography, 92% yield of compound [1a] was achieved.

*Synthesis of PyCh-1 [**1b**]:*

Further, 1 g of compound [1a] was dissolved in 20 ml THF followed by the addition of 1.2 equivalent of hydroiodic acid in a round bottom flask. A yellow coloration was observed and the reaction mass was stirred for 24 hr. The solvent was removed by rotary-evaporator and the final product separated as a solid brown solid powder. (0.75gm, 75% yield). **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ(ppm) 8.85 (s, 1H), 8.39-8.7 (dd, 1H), 7.97-7.95 (dd, 1H,), 7.56-7.49 (m, 3H), 7.40-7.23 (m, 5H). **^{13}C NMR** (100 MHz, DMSO-d$_6$): δ (ppm) 189.53, 144.55, 142.12, 129.64, 128.89, 127.64, 127.56, 124.62, 123.64, 122.95, 121.46, 115.93, 110.67, 110.55. **HRMS (ESI)** m/z: $[M + H]^+$ calcd for 337.0, found 337.16.

*Synthesis of PyCh-2 [**1c**]:*

Compound [1c] was synthesized according to the same procedure as that of [1b] with a minor modification, i.e. instead of hydroiodic acid, hydrobromic acid was taken as the starting material. [1c] was obtained as a solid powder compound (0.74 g, 74% yield). **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ(ppm) 9.08 (s, 1H), 8.34-8.31 (dd, 1H), 8.26-8.27 (dd, 1H,), 7.58-7.56 (d, 2H), 7.48-7.32 (m, 4H), 7.25-7.20 (m, 2H). **^{13}C NMR** (100 MHz, DMSO-d$_6$): δ(ppm) 191.29, 141.83, 129.38, 128.80, 127.27, 125.48, 123.26, 122.89, 122.41, 122.06, 120.95, 119.56, 115.74, 110.48.**HRMS (ESI)** m/z: $[M + H]^+$calcd for 290.10 and found 291.0.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7.359
7.331
7.310
7.251
7.231
C
O
NH
I
11
10
9
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3.20
2.13
1.17
2.11

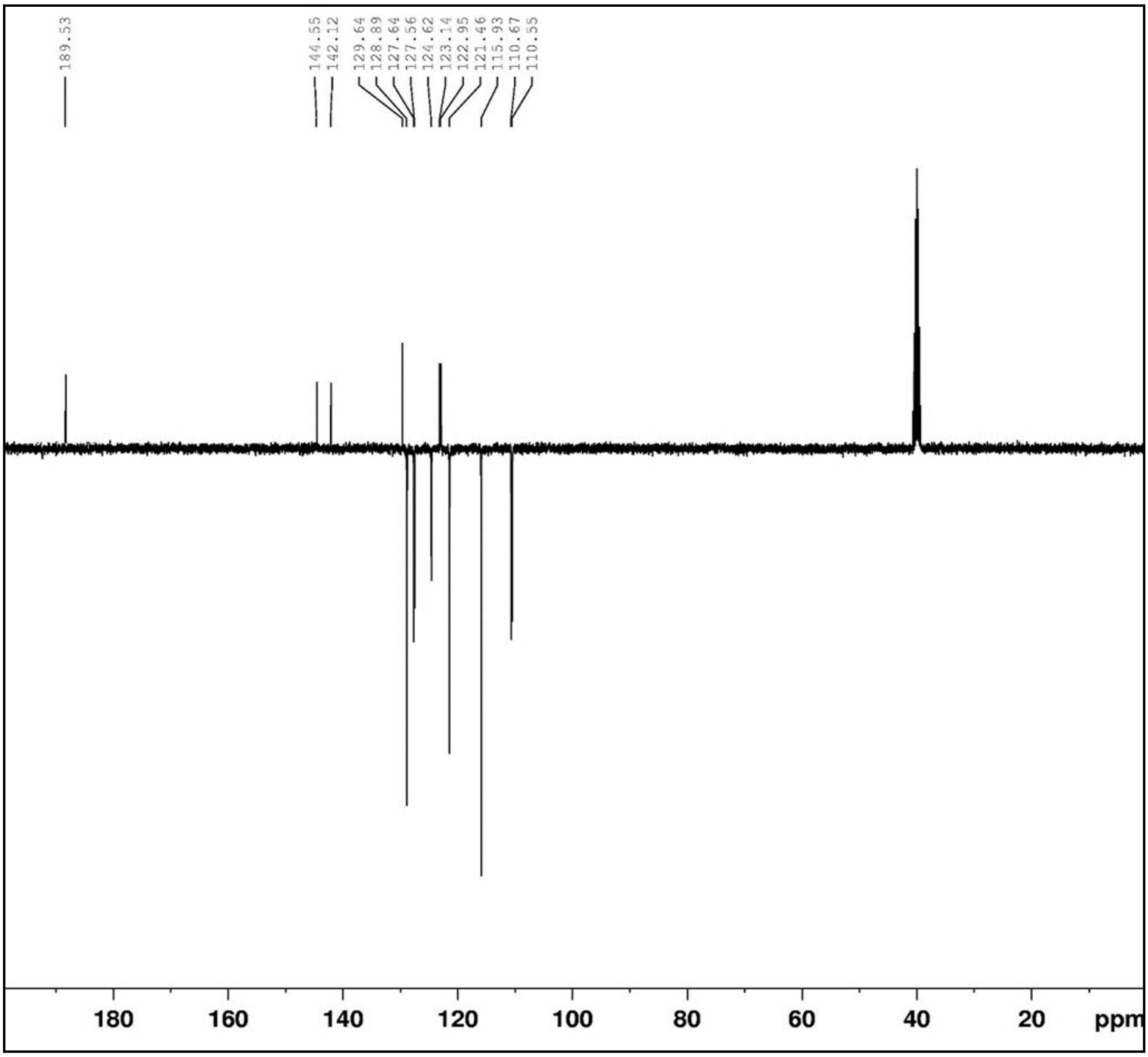
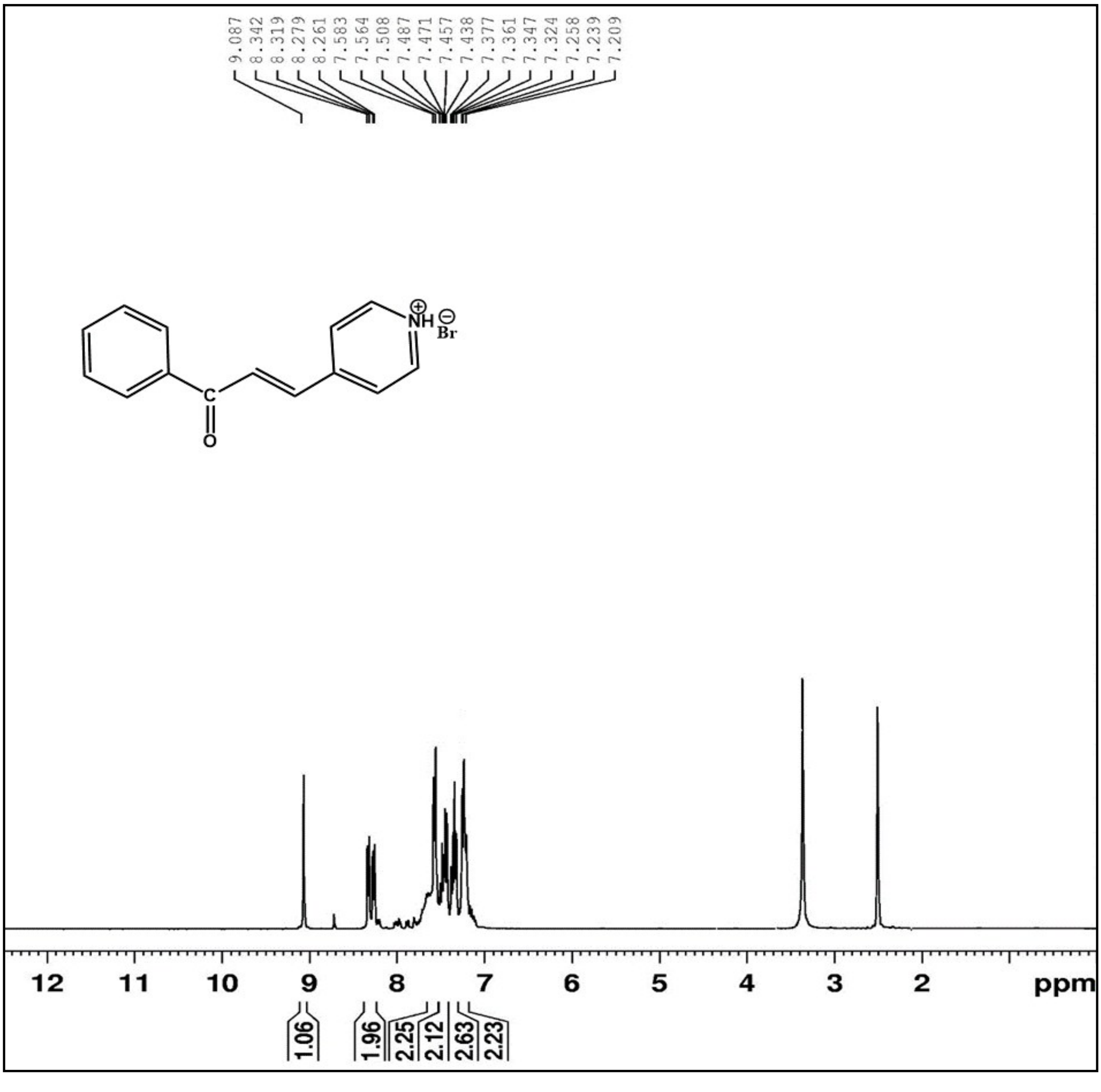


Fig. S1 ^{1}H and ^{13}C NMR spectra of PyCh-1 ionic conductor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7.361
7.347
7.324
7.258
7.239
7.209
NH
Br
C
O
12
11
10
9
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6
5
4
3
2
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2.25
2.12
2.63
2.23

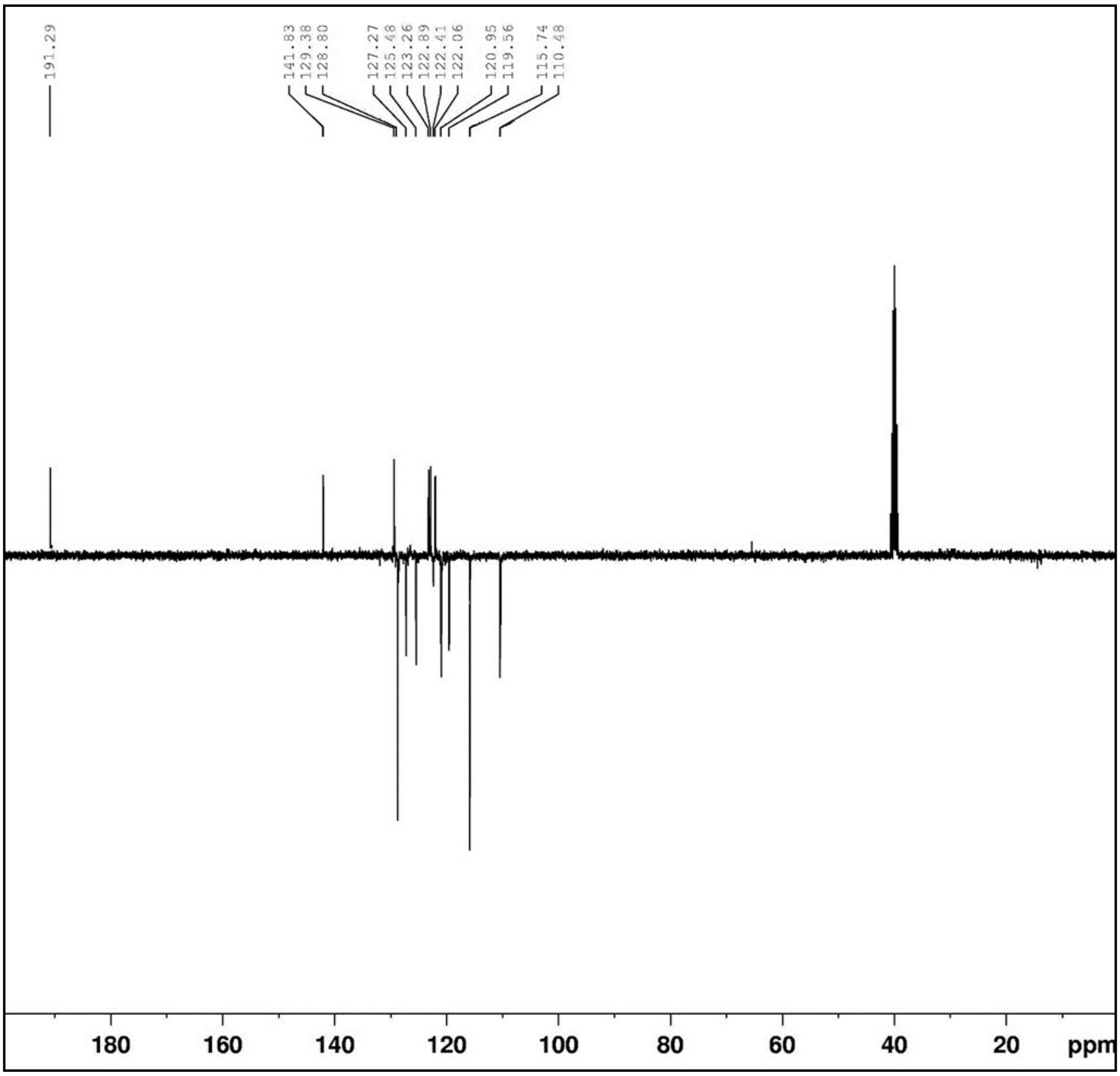


Fig. S2 ^{1}H and ^{13}C NMR spectra of PyCh-2 ionic conductor

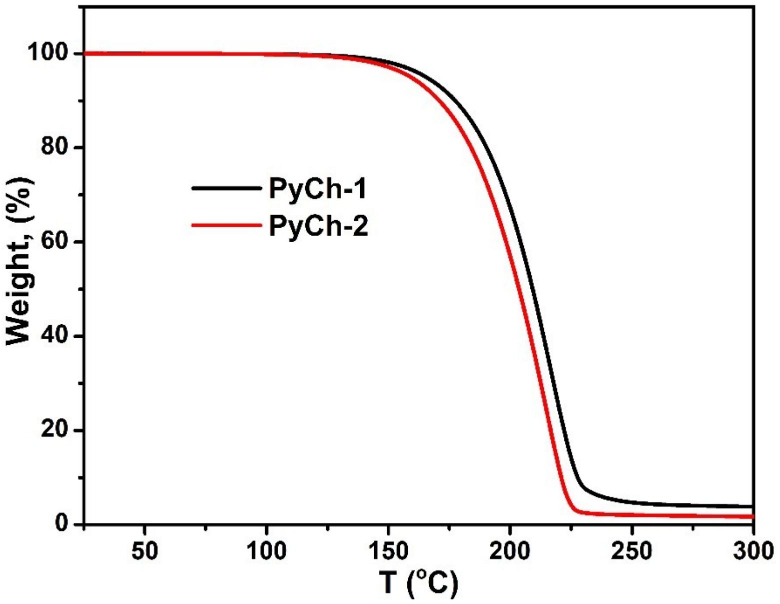
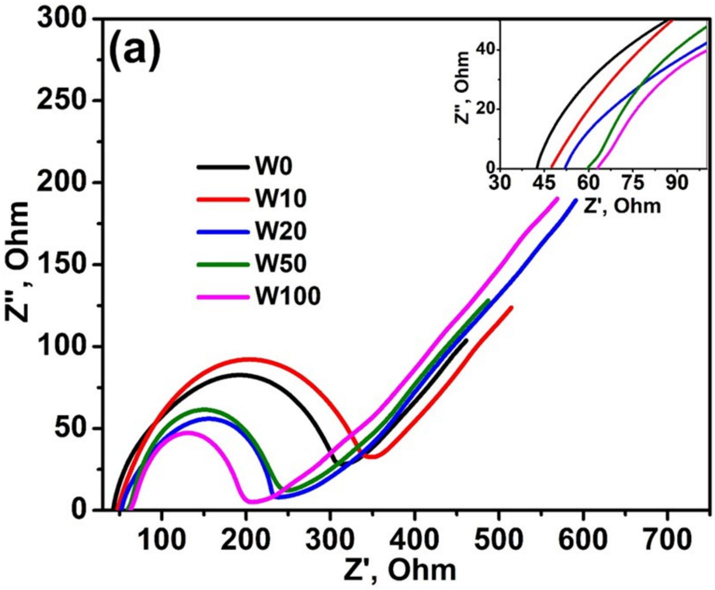


Fig. S3 Thermo-gravimetric analysis (TGA) of organic ionic conductors



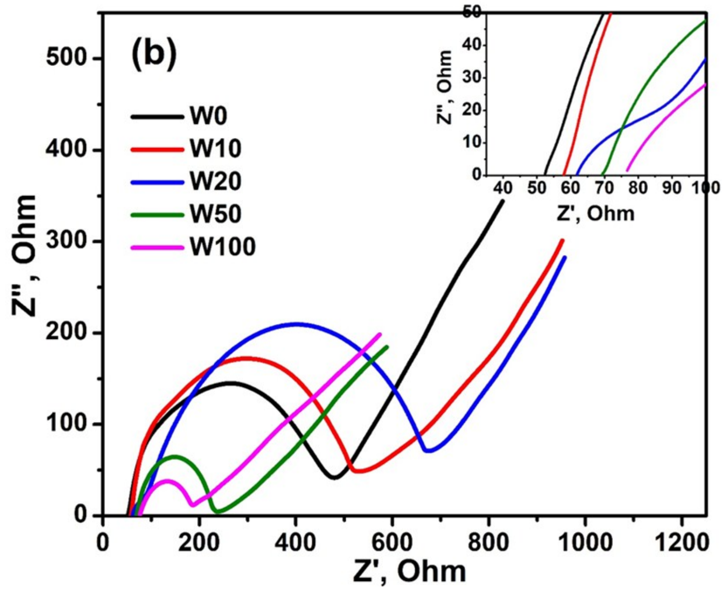


Fig. S4 The nuquist plot of the organic ionic conductors

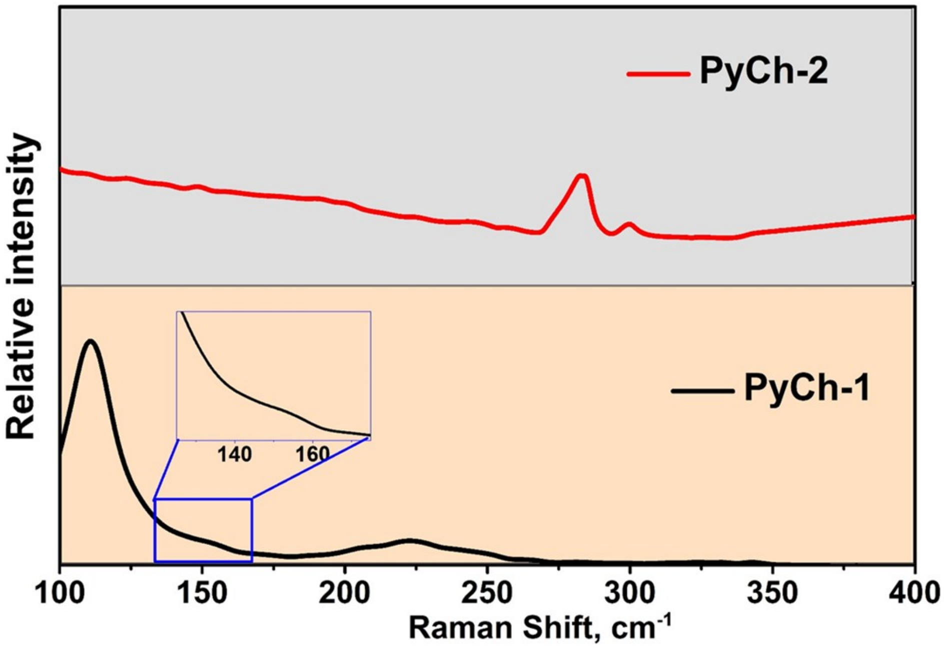


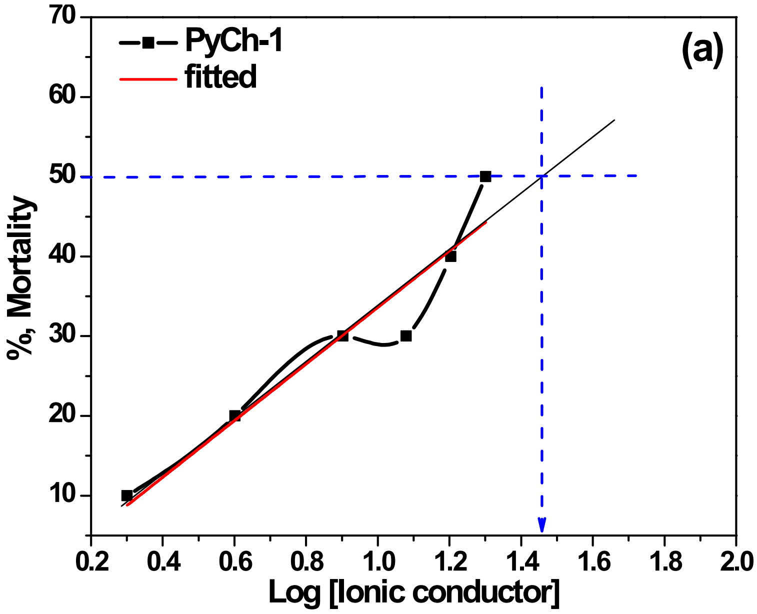
Fig. S5 Raman spectra of organic ionic conductors

Toxicity Screen process (Brine shrimp lethality bioassay)

This both techniques are considered as a valuable tool for initial calculation of toxicity. The growing of brine shrimp, take 0.05gm brine shrimp eggs mixed in artificial seawater and kept 48 hr in incubation at 25˚C. Then take 10 nauplii and 1000 µL artificial sea water were mixed to each vial of a 24 well microtiter plate and make 2.5mL by adding artificial sea water. The each vial having 1mL seawater, 0.45mL organic ionic conductors (PyCh-1 and PyCh-2), 1mL sea water with 10 nauplii and 0.05mL dimethylsulfoxide. Each vial solution three sets was taken measured the LC_{50}. The 24 hr incubation, after calculate dead and live larvae and $LC_{50,}$ was determined for PyCh-1 and PyCh-2 ionic conductors.

Table S1. Toxicity results obtain from Fig. S5, using brine shrimp technique.

[Ionic conductors] (µg/mL)	Log [Ionic conductors]	PyCh-1		PyCh-2	
		% Mortality	LC_{50} (µg/mL)	% Mortality	LC_{50} (µg/mL)
2	0.30103	10		10	
4	0.60206	20		30	
8	0.90309	30	28.57	30	15.99
12	1.079181	30		40	
16	1.2041	40		50	
20	1.30103	50		60	



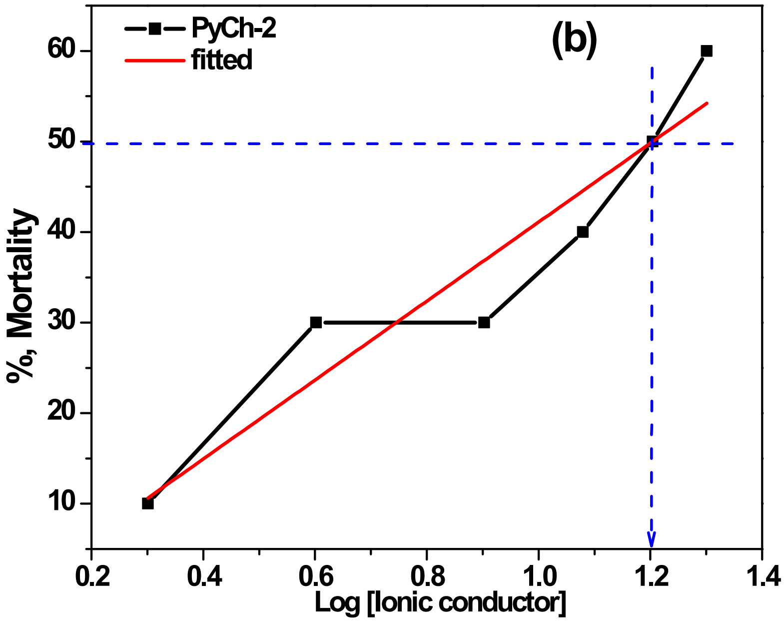


Fig. S6 Toxicity of % Mortality *vs* Conc. of (a) PyCh-1 and (b) PyCh-2 ionic conductors

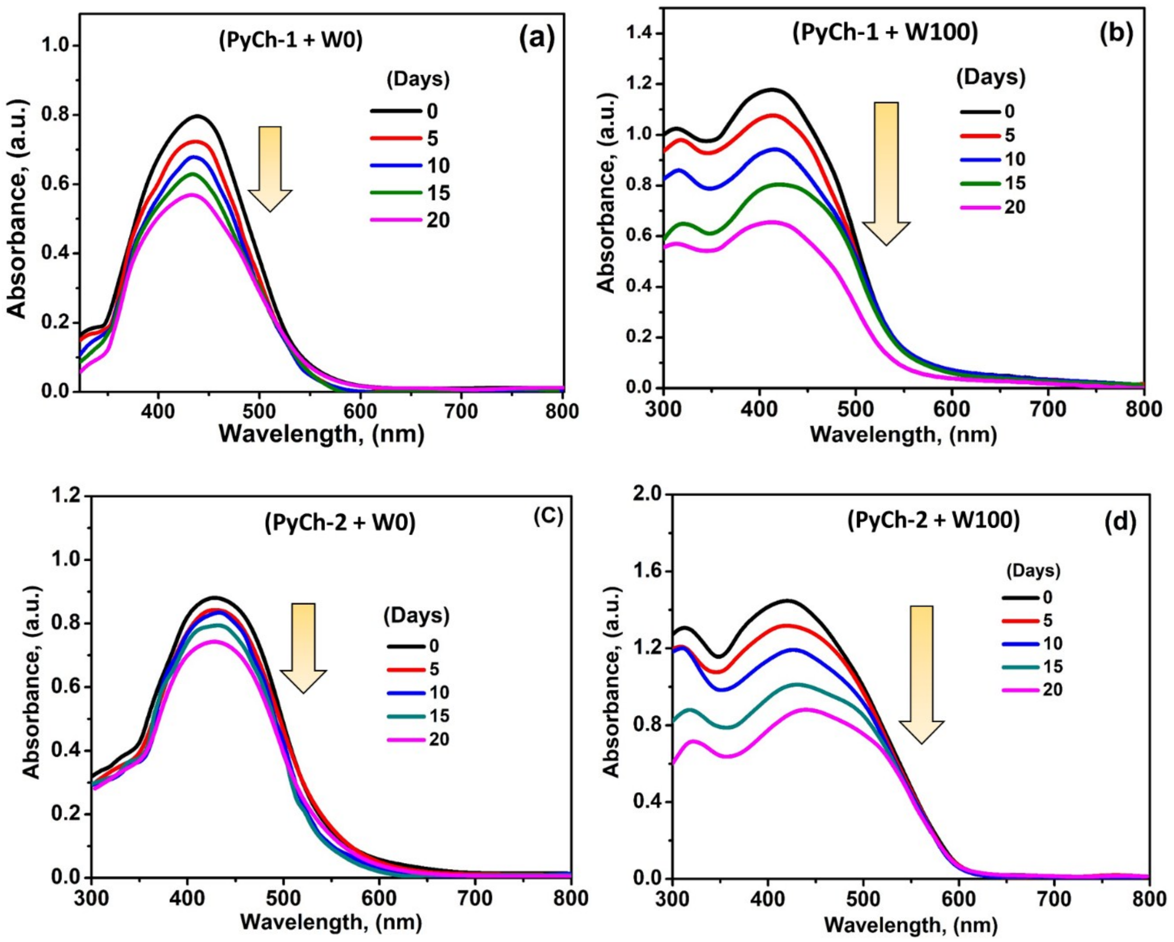


Fig. S7 Absorbance spectra of OICs with W0 and W100 water content devices

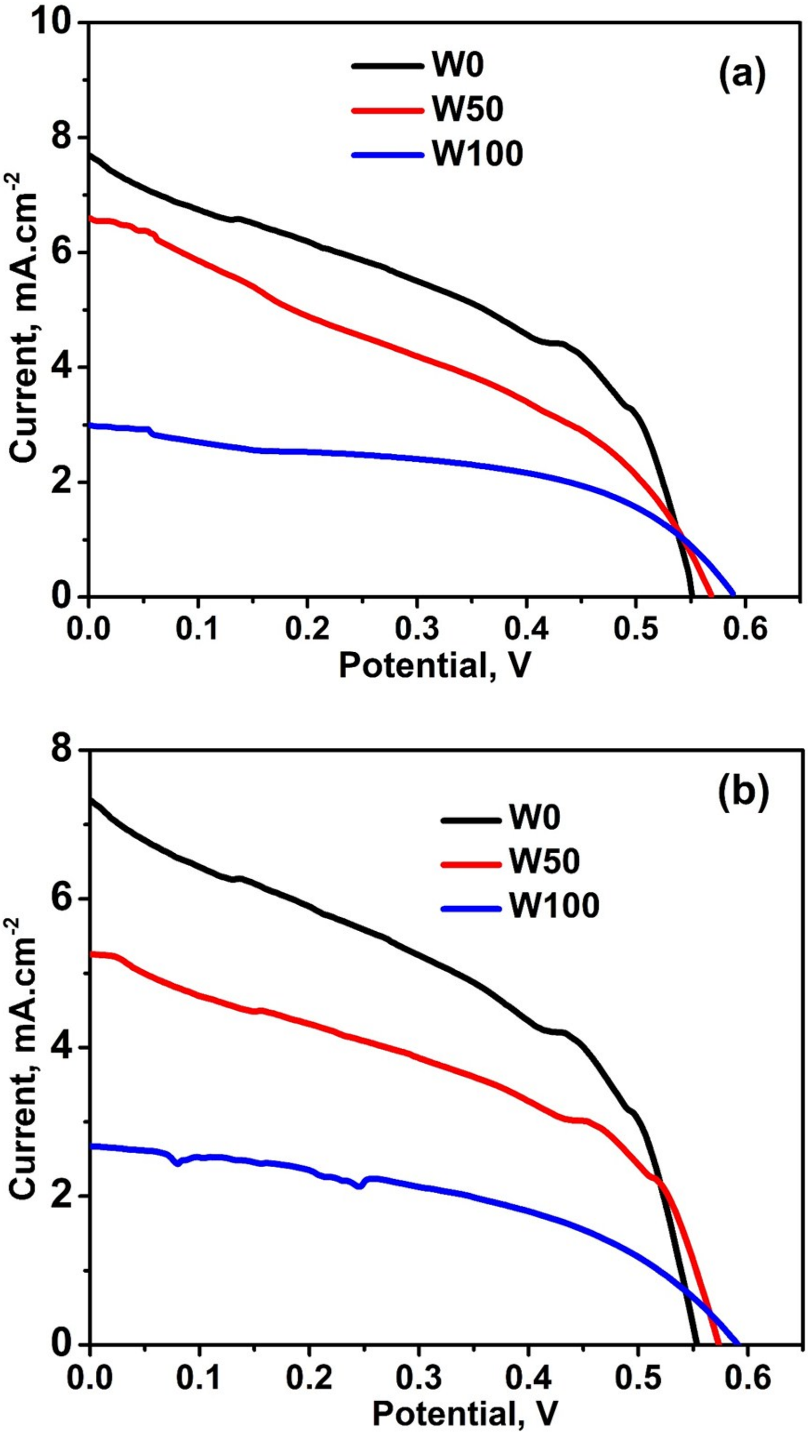


Fig. S8 J-V curve of aqueous DSSCs based on (a) PyCh-1 and (b) PyCh-2 ionic conductor. (Using single component OICs with W0 and W100 water content).

Table S2. Solar cells parameters of DSSC with single component AOICs.

Photovoltaic parameters	**PyCh-1 in water %**			**PyCh-2 in water %**		
	W0	**W50**	**W100**	**W0**	**W50**	**W100**
J_{sc} **(mA.cm^{-2})**	7.7	6.24	2.83	7.33	5.25	2.67
V_{oc} **(mV)**	548	568	588	551	571	637
FF **(%)**	42	36	49	44	46	41
PCE **(%)**	1.9	1.3	0.9	1.8	1.4	0.7

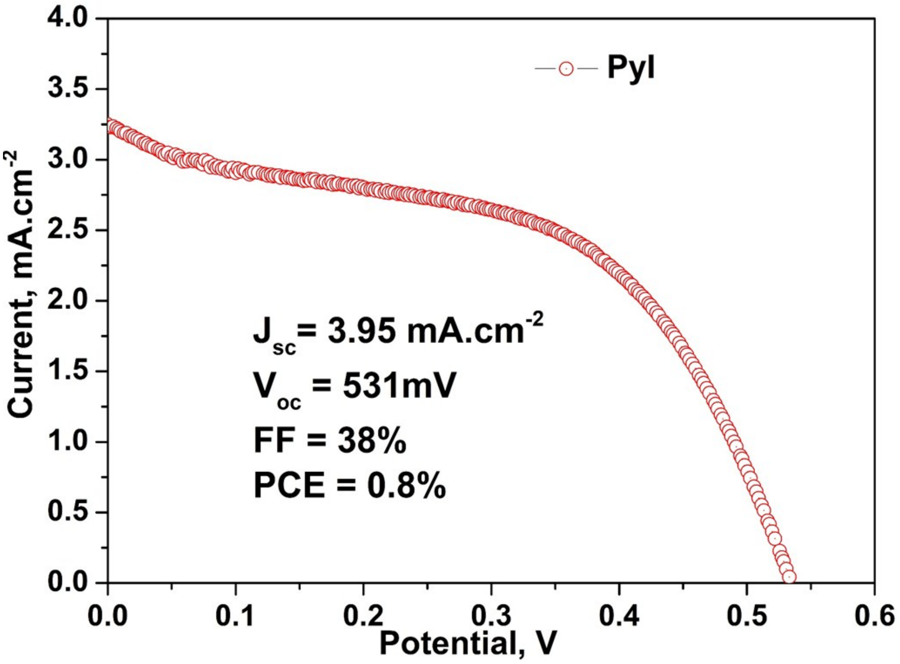


Fig. S9 J-V curve of pyridinum iodide (without any substitution) electrolytes in DSSCs.

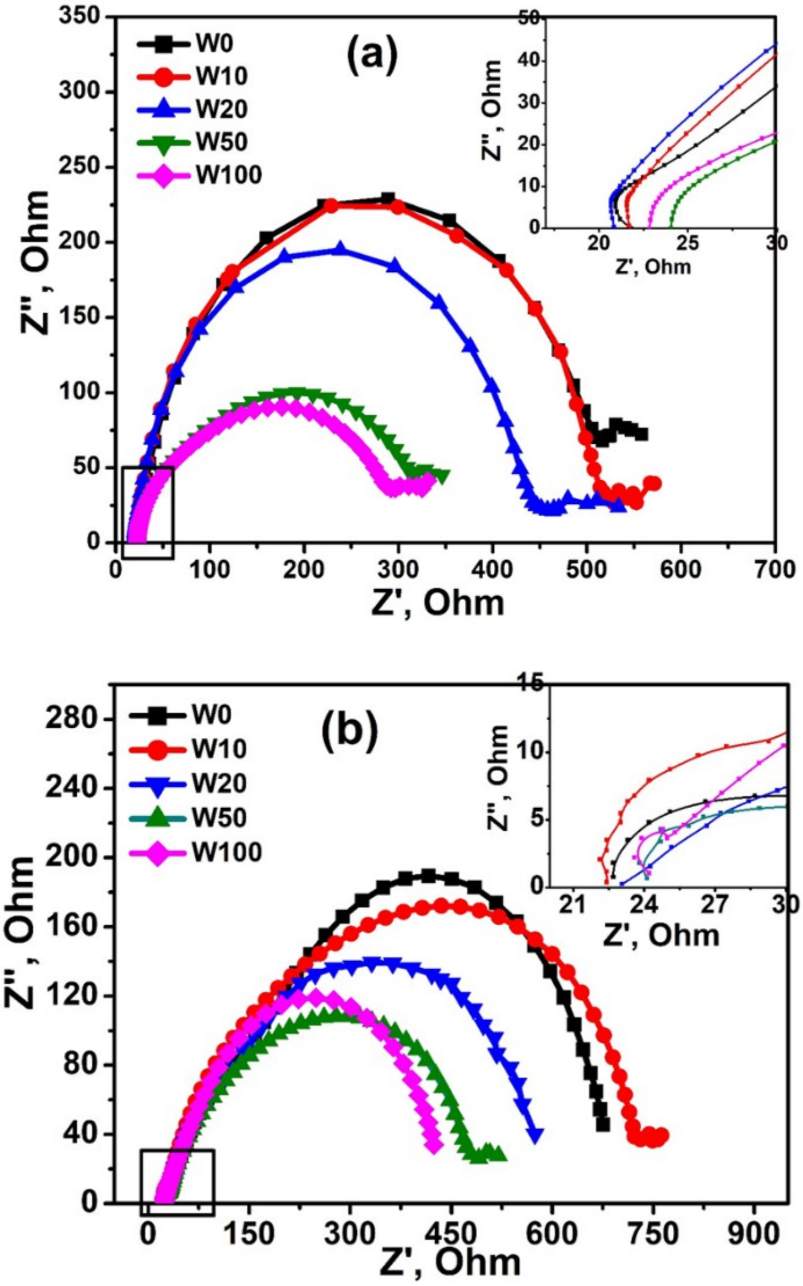


Fig. S10 Nyquist plot (device measured at dark condition) of aqueous DSSCs with AOICs (a) and PyCh-2 (b). (Insets of both figures magnification of high frequency curve)

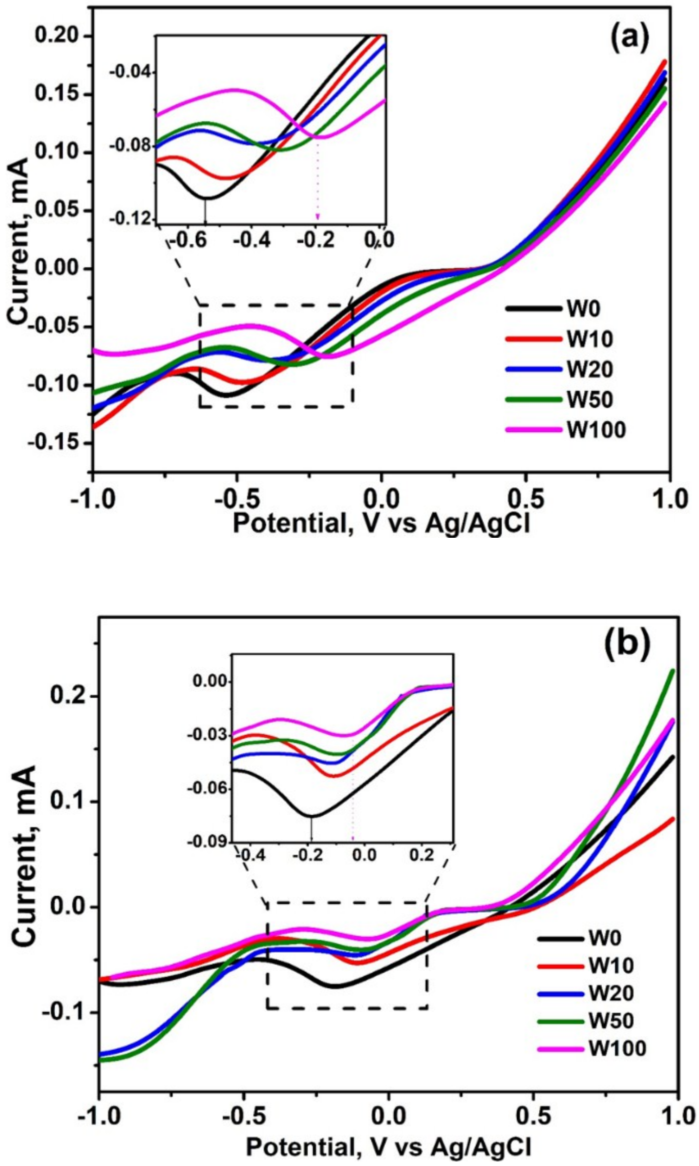


Fig. S11 LSV of different amount of water in electrolytes, (a) PyCh-1 and (b) PyCh-2 ionic conductors.

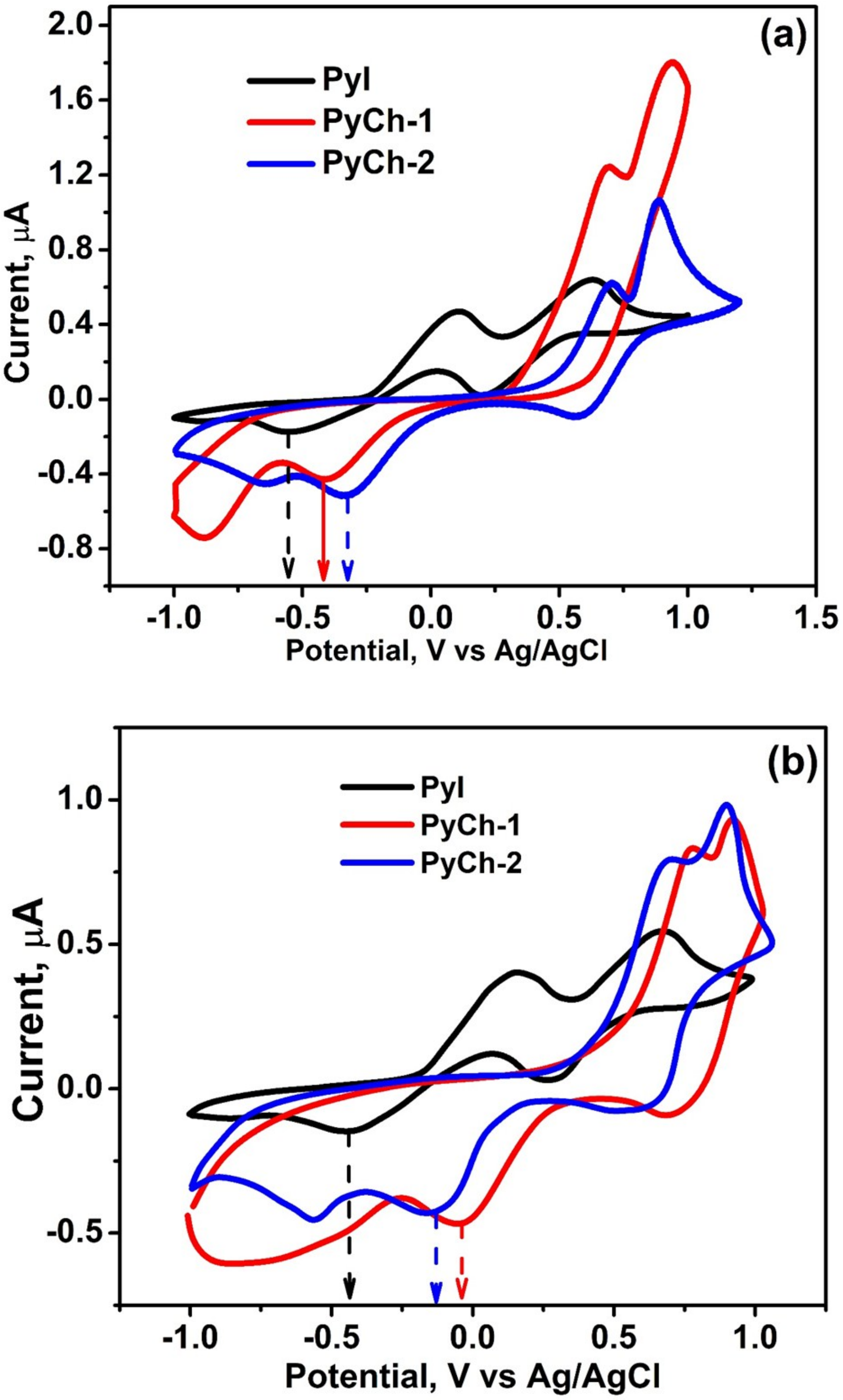


Fig. S12 Cyclic voltammogram of OICs and PyI electrolytes under (a) acetonitrile and (b) water solvents

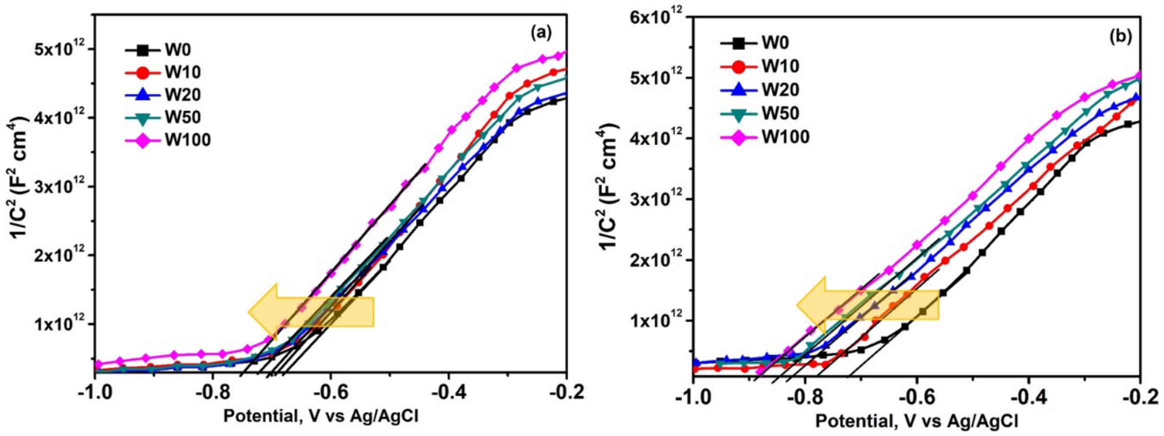


Fig. S13 The Mott-Schottky plots of dye sensitized TiO_2 with different amount of water in PyCh-1 (a) and PyCh-2 (b) electrolytes

Mott-Schottky (MS) analysis were performed with three electrode system. A SK3 dye sensitized TiO_2 thin films were used a working electrode, Non-aqueous Ag/AgCl and Pt-wire were used as a reference and counter electrode, respectively. The MS behaviour of the dye sensitized TiO_2 film with various percentage of water in electrolytes (PyCh-1 and PyCh-2) was obtained to determine their flat-band potential (V_{fb}) as shown in **Fig. S13. [5-6]** The V_{oc} of the cells is determined from the redox potential in the electrolyte and the quasi Fermi level, which increases linearly with V_{fb}. A negative shift (-0.67 to -0.75V in PyCh-1 and -0.72 to -0.88 in PyCh-2 electrolyte) of V_{fb} of TiO_2 with increase amount of water. The V_{fb} was calculated on extrapolating the straight lines to x-axis ($1/C^2 = 0$).

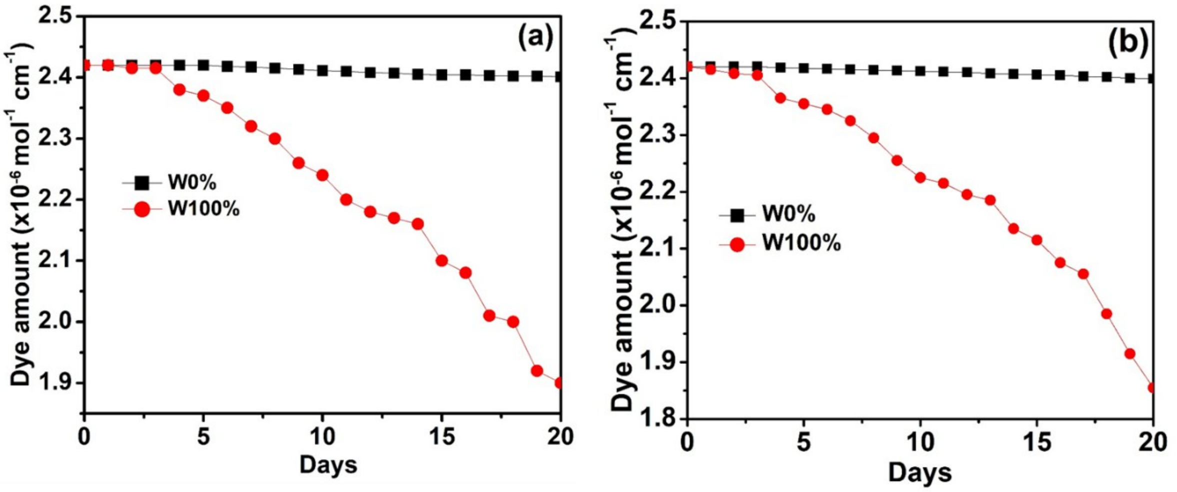


Fig. S14 Dye desorption on TiO_2 surface under W100 (with) and W0 (without) water content in OICs.

Table R1. Calculated percentage of dye desorption with different percentage of water content electrolyte

Electrolytes		W0		W100	
	0 day/% of desorption, (*mol^{-1} cm^{-1}*)	10days/% of desorption, (*mol^{-1} cm^{-1}*)	20 days/% of desorption, (*mol^{-1} cm^{-1}*)	10days/% of desorption, (*mol^{-1} cm^{-1}*)	20 days/% of desorption, (*mol^{-1} cm^{-1}*)
PyCh-1	2.42×10^{-6}	2.41×10^{-6} **(0.41%)**	2.40×10^{-6} **(0.82%)**	2.24×10^{-6} **(7.41%)**	1.90×10^{-6} **(21.48%)**
PyCh-2	2.42×10^{-6}	2.40×10^{-6} **(0.82%)**	2.39×10^{-6} **(1.23%)**	2.22×10^{-6} **(8.26%)**	1.85×10^{-6} **(23.55%)**

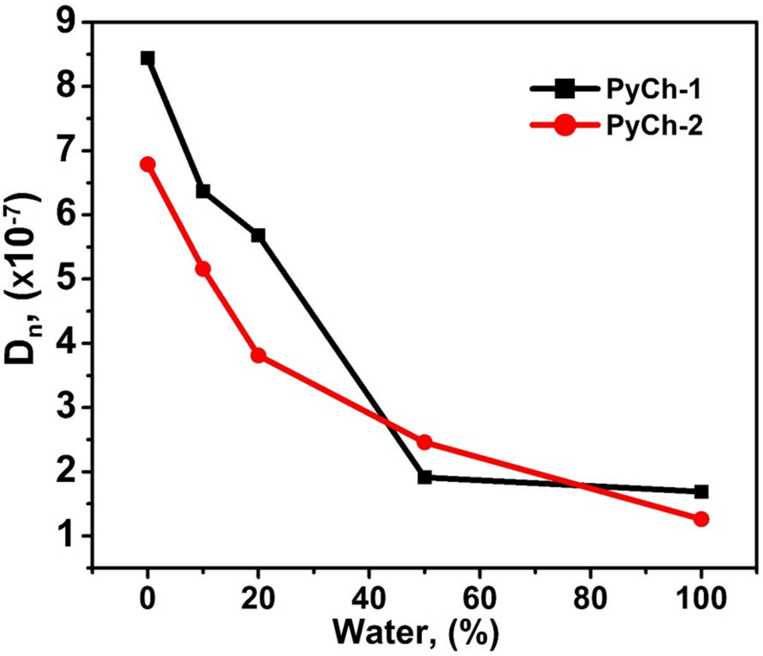
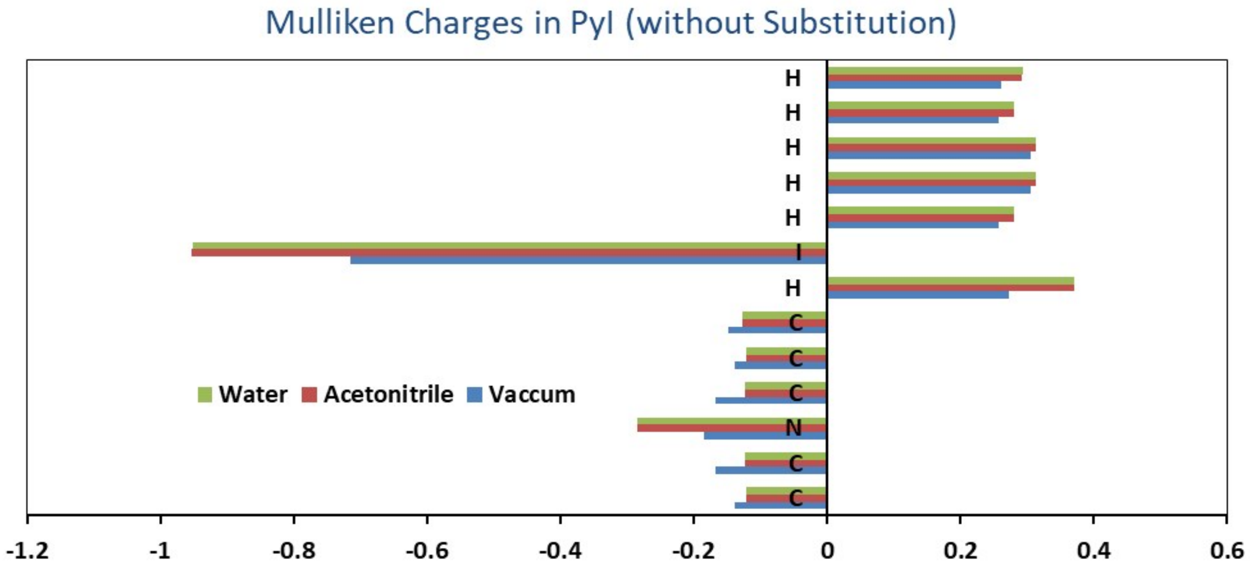


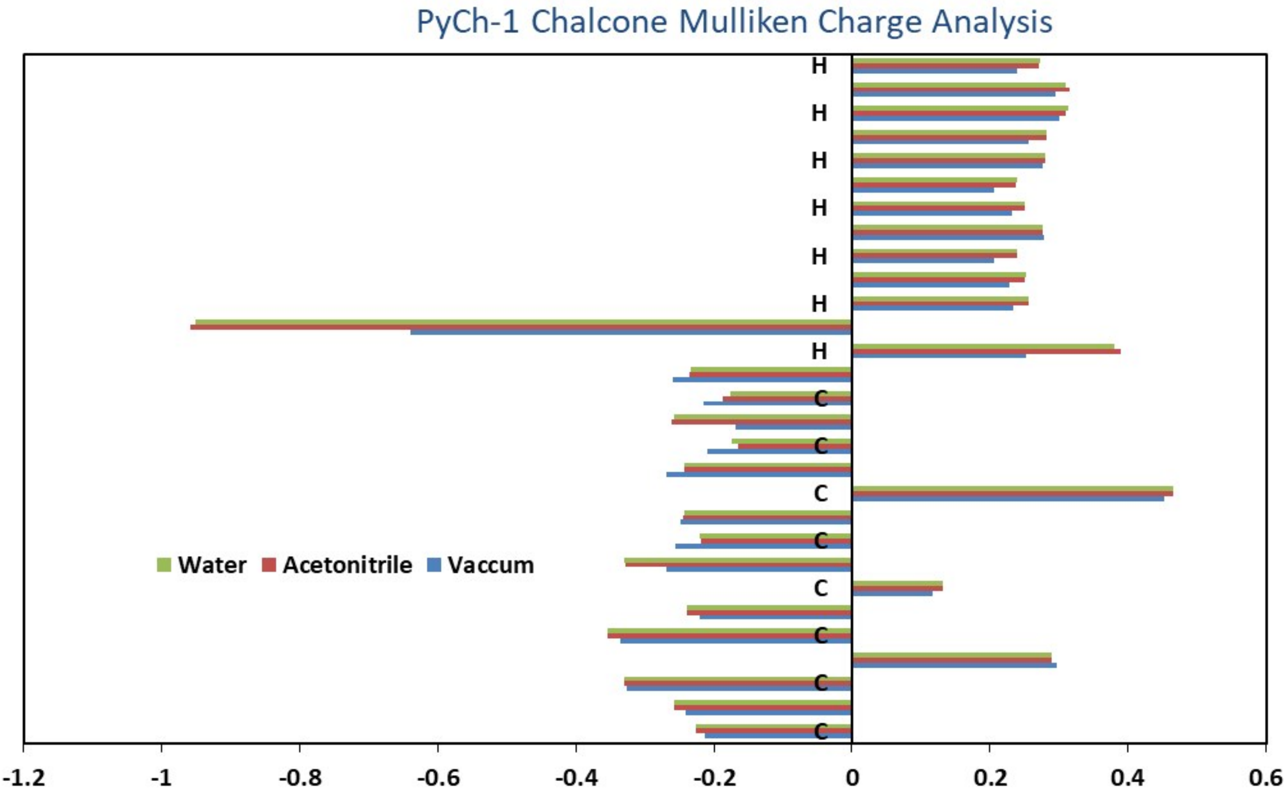
Fig. S15 Diffusion coefficient of various amount of water content electrolyte

The diffusion coefficient calculated using following equation;

$$D_n = L^2/(W_s - T) \qquad (2)$$

Here, *L, R, S* and *Ws-T* represent thickness between two symmetric Pt-FTO electrode, resistance of ionic conductors, and active surface area of the electrode and finite Warburg impedance, which is determined by fitting impedance spectra.


Mulliken Charges in PyI (without Substitution)


PyCh-1 Chalcone Mulliken Charge Analysis

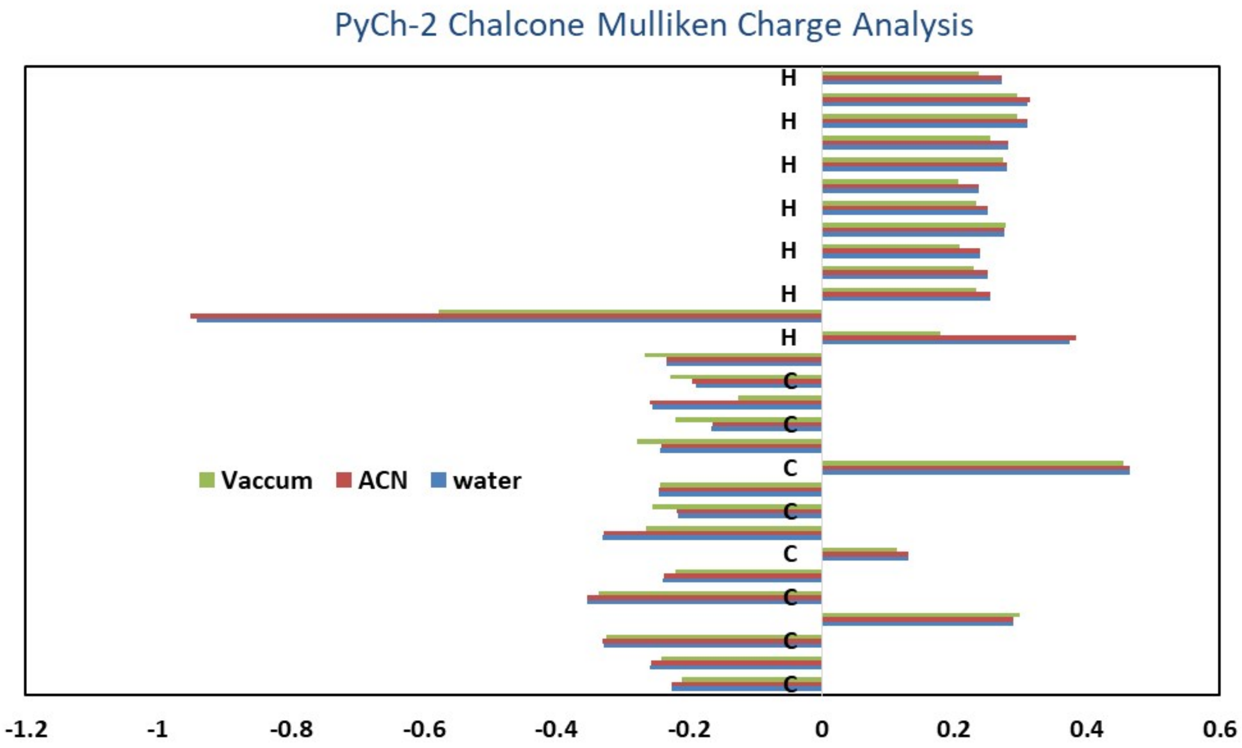


Fig. S16 Mulliken charge of OICs and un-substituted PyI (reference electrolyte) under vacuum, acetonitrile and water solvents

Table S3. Mulliken charge of PyI (without substituted) reference ionic conductor

Atom	Vacuum	Acetonitrile	Water
C	-0.13879	-0.121365	-0.12157
C	-0.16743	-0.122799	-0.12307
N	-0.18386	-0.285227	-0.28482
C	-0.1674	-0.122796	-0.12307
C	-0.13882	-0.121365	-0.12157
C	-0.14726	-0.127436	-0.12747
H	0.273239	0.372107	0.371272
I	-0.71559	-0.952612	-0.95179
H	0.256867	0.280839	0.281108
H	0.30536	0.313372	0.313227
H	0.30531	0.313371	0.313227
H	0.256866	0.280838	0.281108
H	0.261506	0.293073	0.293423

Table S4 Mulliken charge of PyCh-1

Atom	Vaccum	Acetonitrile	Water
C	-0.21219	-0.225898	-0.22637
C	-0.24018	-0.257119	-0.25762
C	-0.32596	-0.329184	-0.3295
C	0.297534	0.28969	0.289422
C	-0.3357	-0.353229	-0.35373
C	-0.21999	-0.238358	-0.23901
C	0.117179	0.131283	0.131773
O	-0.2693	-0.328297	-0.3304
C	-0.25604	-0.218212	-0.21982
C	-0.24839	-0.244457	-0.24324
C	0.451961	0.4655	0.464839
C	-0.26892	-0.242248	-0.2436
C	-0.21026	-0.164855	-0.17398
N	-0.1687	-0.26158	-0.25663
C	-0.21573	-0.186701	-0.17686
C	-0.25967	-0.235925	-0.23311
H	0.25234	0.389564	0.380373
I	-0.63973	-0.958393	-0.95091
H	0.233134	0.254943	0.255389
H	0.228735	0.251089	0.251598
H	0.206127	0.238999	0.240013
H	0.278663	0.276507	0.276343
H	0.232396	0.250846	0.251197
H	0.205737	0.237883	0.238361
H	0.275987	0.27969	0.279815
H	0.256462	0.281991	0.282497
H	0.299691	0.310517	0.31255
H	0.295053	0.314416	0.308734
H	0.239758	0.271538	0.271886

Table S5. Mulliken charge of PyCh-2

Atom	water	acetonitrile	Vaccum
C	-0.22631	-0.22595	-0.21129
C	-0.25777	-0.25699	-0.24082
C	-0.32902	-0.32928	-0.32471
C	0.289827	0.289671	0.298754
C	-0.35392	-0.35306	-0.33486
C	-0.23909	-0.23834	-0.22021
C	0.130851	0.131354	0.114722
O	-0.33048	-0.32806	-0.26385
C	-0.2171	-0.21827	-0.25572
C	-0.24521	-0.24482	-0.2429
C	0.464595	0.465544	0.45489
C	-0.24266	-0.24205	-0.27761
C	-0.16612	-0.16375	-0.22085
N	-0.25491	-0.25912	-0.12633
C	-0.18897	-0.19507	-0.22845
C	-0.23277	-0.23405	-0.26566
H	0.37342	0.384841	0.17958
Br	-0.94141	-0.95095	-0.57723
H	0.255404	0.255038	0.233067
H	0.251676	0.25113	0.229307
H	0.239659	0.238704	0.207827
H	0.276312	0.276532	0.278213
H	0.251267	0.250848	0.232661
H	0.237233	0.237419	0.206568
H	0.280017	0.280271	0.273419
H	0.282298	0.282153	0.253831
H	0.310865	0.310475	0.294519
H	0.310443	0.314275	0.295714
H	0.271879	0.271484	0.237428

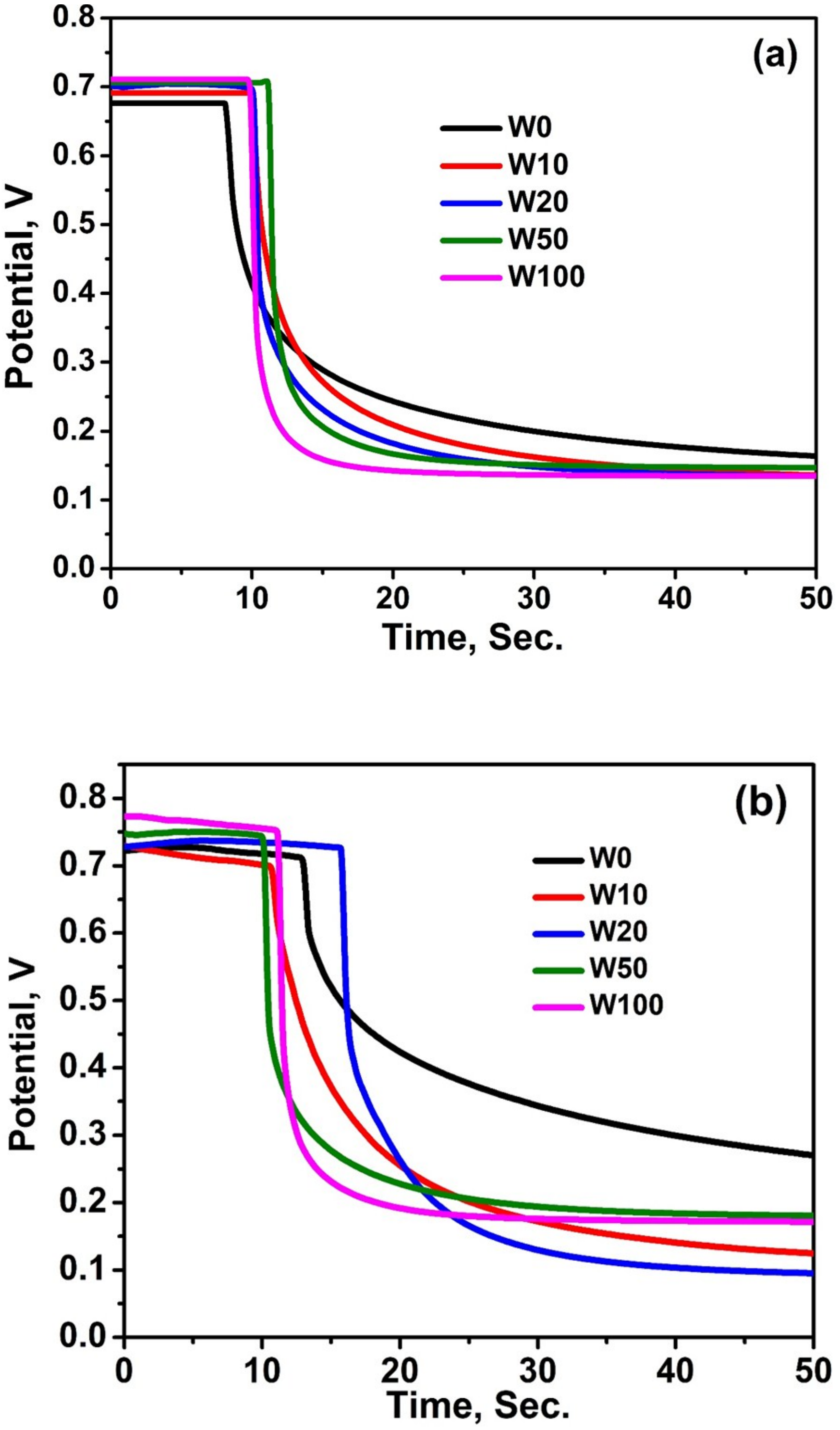


Fig. S17 OCVD curves of the aqueous DSSCs with different water content electrolytes (a) PyCh-1 and (b) PyCh-2

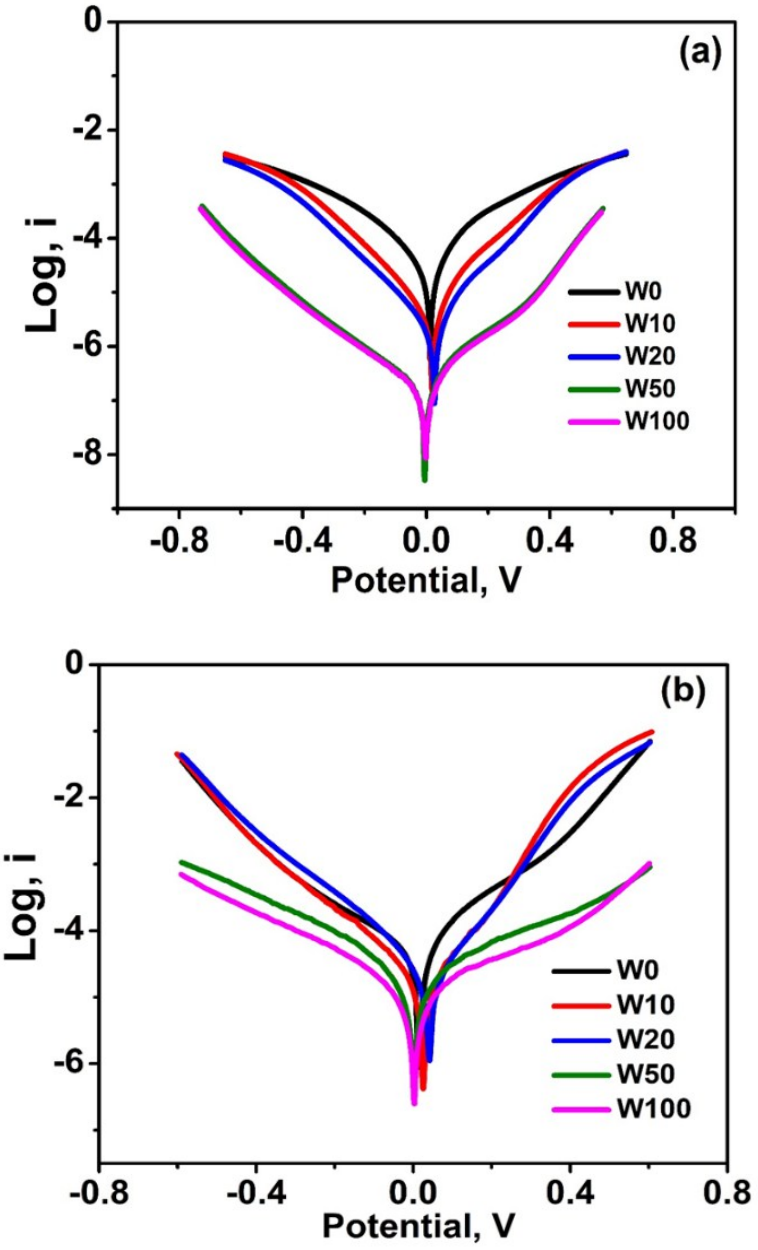
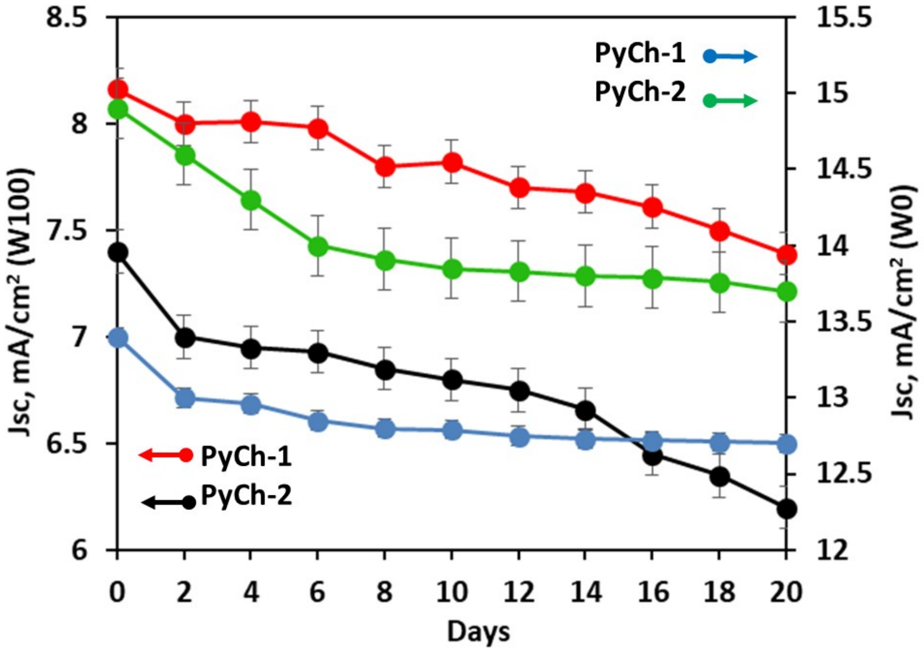


Fig. S18 Tafel polarization curves of DSSCs based on the various amount of water in electrolytes, (a) PyCh-1 and (b) PyCh-2. The measurement under dark condition and 0.05mV/s scan rate



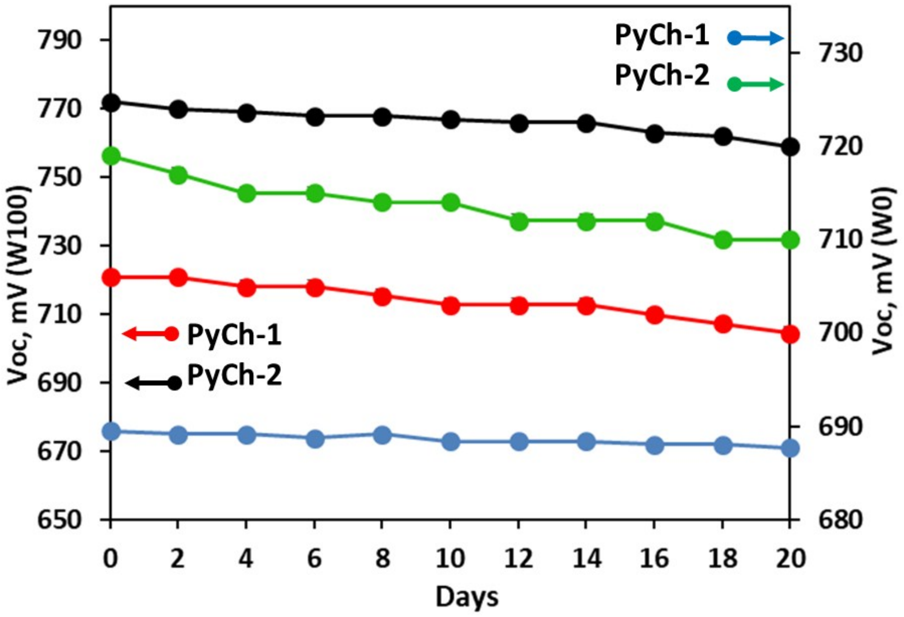


Fig. S19 Stability of photovoltaic parameters (J_{sc} and V_{oc}) in W0 and W100 water content in PyCh-1 and PyCh-2 ionic conductor.

References

(1) S. S. Soni, K. B. Fadadu, J. V. Vaghasiya, B. G. Solanki, K. K. Sonigara, A. Singh, D. Das and P. K. Iyer, *J. Mater. Chem. A*, 2015, **3,** 21664-21671.

(2) J. V. Vaghasiya, K. K. Sonigara, K. B. Fadadu and S. S. Soni, *Perspectives in Science* 2016, **8,** 46-49.

(3) J. V. Vaghasiya, K. K. Sonigara, J. Prasad, T. Beuvier, A. Gibaud and S. S. Soni, *J. Mater. Chem. A*, 2017, **5,** 5373-5382.

(4) X. Y. Yang, Y. X. Jia, W. S. Tay, Y. Li, S. A. Pullarkat and P. H. Leung, *Dalton Trans*. 2016, **45,** 13449-13455.

(5) J. Bandara and U.W. Pradeep, *Thin Solid Films* 2008, **517**, 952.

(6) W. Zhang, L. Qiu, X. Chen, F. Yan, *Electrochimica Acta* 2014, **117**, 48.