Supporting Information

Lindqvist polyoxometalates as Electrolyte in p-type Dye Sensitized Solar Cells

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Materials and Methods

Materials

Sodium molybdate dihydrate (≥99.5 %), Sodium tungstate dihydrate (≥99 %) (Tetrabutylammonium Bromide (≥98 %), Acetic Anhydride (≥98 %), Hydrochloric acid (≥37 %) was purchased from Sigma-Aldrich and were used without any further purification.

Instrumentation

UV–Vis spectra were recorded on a Hewlett Packard 8453 UV-visible spectrophotometer.

Cyclic voltammetry and Differential Pulse voltammetry experiments were performed using an Autolab pgstat128N potentiostat with a glassy carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode. All electrochemistry experiments were performed under aerobic conditions. Potentials given in NHE were calculated by adding 0.06V to the measured potential vs Ag/AgCl. This number was obtained by calibration of the Ag/AgCl electrode vs the Fc/Fc$^+$ redox couple.

Current-voltage (I-V) characteristics were using measured using an Eco Chemie 6-stat potentiometer under simulated AM1.5G irradiation using a 100 W Xe lamp solar simulator (Oriel LCS-100). The light intensity was adjusted with an NREL-calibrated Si reference solar cell and quartz window The illuminated area of 0.785 cm^2 was defined by a photomask with an aperture.

Synthesis of Polyoxometalates

Mo_6O_{19}

sodium molybdate dihydrate (10.9 g, 45 mmol) of was dissolved in water (40 mL) in a 100 mL Erlenmeyer flask. 6ml of hydrochloric acid was added and the solution turned blue. 5.0 g of tetrabutylammonium bromide was dissolved in 8 ml Milli–Q water and added to the Erlenmeyer, which resulted in immediate white precipitation. The suspension was heated to 100 °C for one hour, during which it slowly changed colour to yellow. The product was filtered and washed three times with 50 ml of Milli–Q water. The solids were dissolved in 250 ml of boiling acetone and placed in a freezer at -20 °C to yield yellow crystals overnight. The solution was decanted and the crystals were washed twice with 100 ml of diethylether. The crystals were then dried under vacuum. Yield is 10.0 g (98% based on Molybdenum)

W_6O_{19}

15.9 g (48 mmol) of sodium tungstate dehydrate was dissolved in 15 ml of acetic anhydride and 12 ml of dimethylformamide in a 100 ml Erlenmeyer flask. The solution was heated to 100 °C for two and a half hours. 10 ml of acetic anhydride, 9 ml of hydrochloric acid and 20 ml of DMF were added to a 100 ml measuring beaker, and the content was added to the Erlenmeyer. A cloudy suspension was formed, which was filtered. The filtrate was collected and stirred vigorously. To another 100 ml beaker, 5.1 g of tetrabutylammonium bromide was dissolved in 20 ml of methanol, which was subsequently added to the stirring filtrate. The suspension that formed was filtered and washed three times with 50 ml of methanol. The white powder that was collected was dissolved in a minimal amount of hot dimethylsulfoxide and placed in a freezer at -20 °C overnight to yield colourless diamond shaped crystals. Yield is 7.1 g (47% based on Tungsten)

Device preparation

2.2 mm thick fluorine doped tin oxide coated glass slides with a surface resistivity of 7Ω sq^{-1} purchased from Sigma Aldrich were used for both the working electrode and the counter electrode. The glass was cut in pieces of 5 cm by 2 cm. On this glass plate a circle with a radius of 0.5 cm made from Ni-Nanoxide N/SP purchased from solaronix was screenprinted. This was followed by sintering at 300 °C using a heat gun for 30 minutes. This plate was then soaked for 24 hours in an 0.3 mM acetonitrile solution containing the P1 dye, which was synthesized according to a literature procedure and shown below[1]. Onto the counter electrode a solution of $PtCl_6$ in isopropanol (2 mg ml^{-1}) was drop casted. This plate was then sintered with the same procedure as the working electrode. Both the electrodes were then screwed onto the Teflon piece (shown below) and secured into position using four O-rings and two metal plates (shown below). Between measurements the compartment was rinsed with acetonitrile.

The electrolytes were prepared as shown in Table 1. The electrolyte of entry 3 was prepared by combining 10 mM LiI and 1 mM I_2. The electrolyte of entry 4 was prepared by using a 1.0 M LiI and 0.1 M I_2.

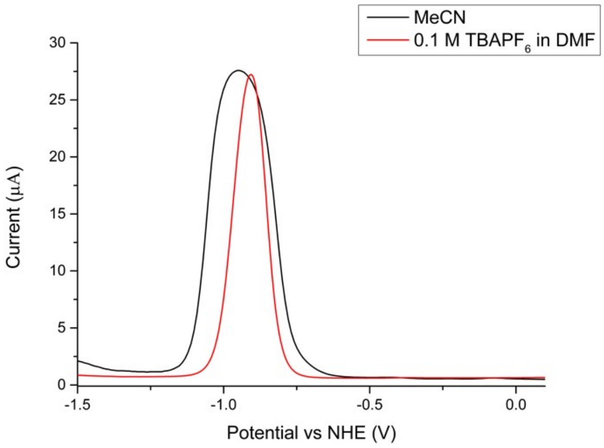


Figure 1 Differential Pulse Voltammogram of the W-POM under different conditions.

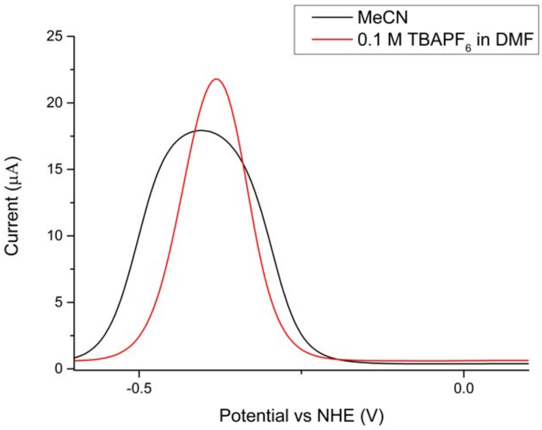


Figure 2 Differential Pulse Voltammogram of the Mo-POM under different conditions.

Table 1 Extended table of photovoltaic parameters for p-type DSSCs prepared in this work. Data was obtained from I–V curve measurements performed AM1.5 solar irradiation (100 mW cm-2). *0.5M of LiTFSI was present as supporting electrolyte. The data shown are the average and the standard deviation of at least 5 different experiments.

Entry	Electrolyte	V_{oc} (mV)	I_{sc} (mA/cm²)	FF	Efficiency
1	0.01M $[TBA]_2Mo_6O_{19}{}^*$	423 ± 28	0.021 ± 0.002	0.13 ± 0.02	0.0012%
2	0.01M $[TBA]_2W_6O_{19}{}^*$	541 ± 34	0.010 ± 0.001	0.11 ± 0.02	0.0006%
3	0.01M I_3^-/I^{-*}	100 ± 5	0.032 ± 0.003	0.23 ± 0.01	0.0007%
4	1.0M I_3^-/I^-	144 ± 14	0.107 ± 0.013	0.31 ± 0.02	0.0048%
5	1.0M I_3^-/I^- (Literature)[25]	106	3.010	0.37	0.12%
6	$Co(tbpy)_3$ (Literature)[26]	80	0.26	0.26	0.006%

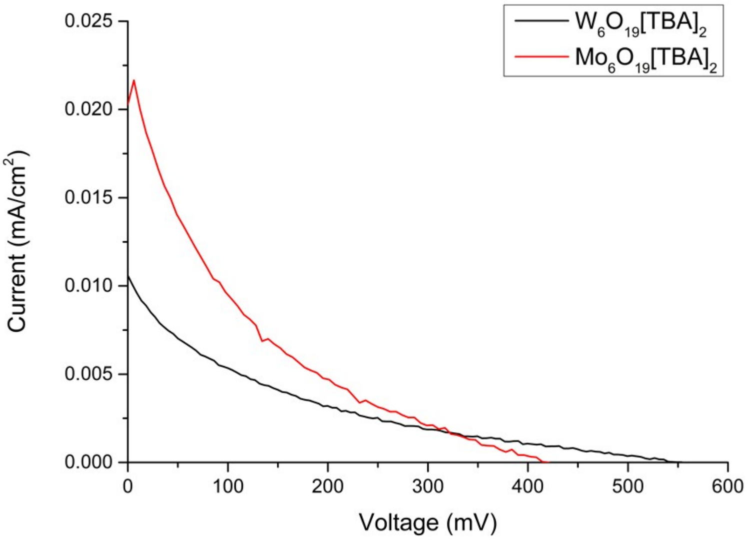


Figure 3 IV Curves measured under AM1.5 Sun of the system solar cell of both POM electrolyte systems

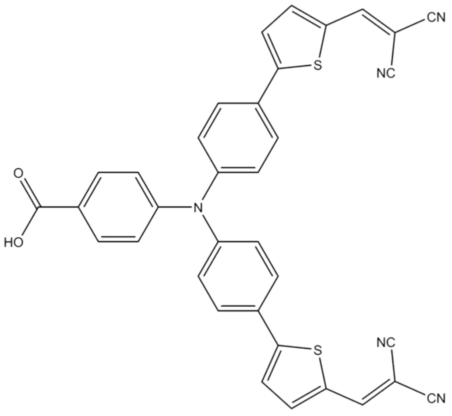


Figure 4 P1 dye structure[1]

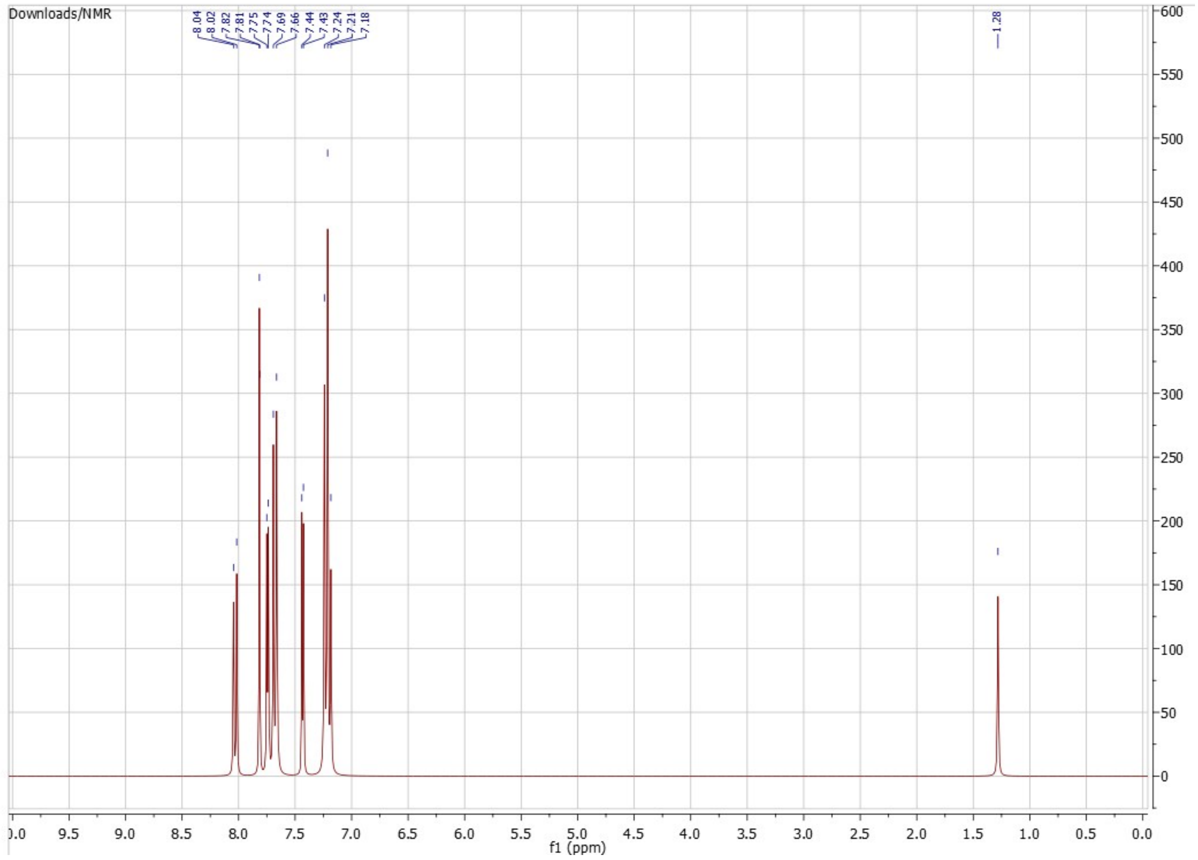
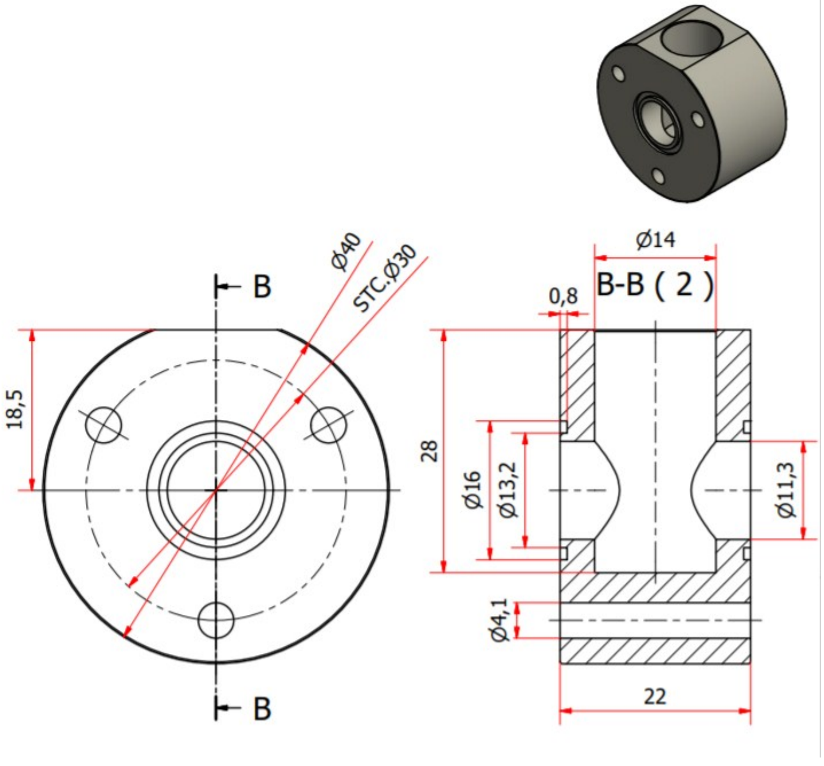
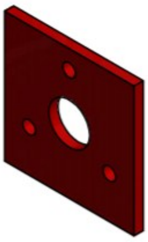
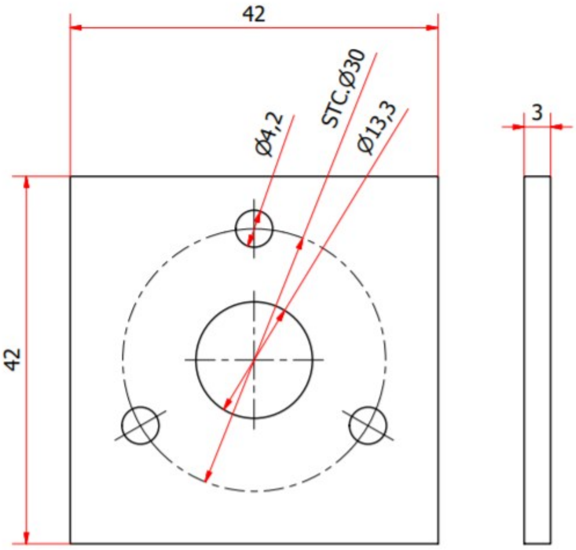


Figure 5 ^{1}H-NMR of P1 dye measured in $CDCl_3$ on 300MHZ Bruker system

1. Qin, P., Zhu, H., Edvinsson, T., Boschloo, G., Hagfeldt, A., & Sun, L. (2008). Design of an organic chromophore for P-type dye-sensitized solar cells. *J. Am. Chem. Soc.*, *130*(27), 8570–8571. https://doi.org/10.1021/ja8001474



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