Supporting Information

Low-cost p-type dye-sensitized solar cells based on Dawson-type transition-metal-substituded polyoxometalates inorganic cosensitizers

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Experimental Section

Material Preparation

All the reagents and chemicals were purchased commercially and used without further purification. $P_2W_{17}Co$ and $P_2W_{17}Mn$ were synthesized according to the reported method[S1].

Sloar Cell Fabrication

FTO conductive glass was ultrasonically cleaned with surfactant, isopropanol, ethanol and dried with N_2. The photocathode film was prepared by screen-printing NiO paste on the clean substrate. Three layers of paste was deposited on the FTO glass to control the thickness of NiO working electrode. Layers then sintered at 350 °C for 5 min, 400 °C for 5 min, and 450 °C for 30 min. When cooled to room temperature, the film was immersed in 0.03 M $P_2W_{17}Co$ DMSO solution, 0.03 M $P_2W_{17}Mn$ DMSO solution and a mixture DMSO solution of 0.03 M $P_2W_{17}Co$ with 0.015 M $P_2W_{17}Mn$ for 24 h, followed by rinsing with ethanol and drying with N_2. The electrolyte is

composed of 1.0 M LiI and 0.1 M I_2 in anhydrous acetonitrile. The solar cells were assembled by sandwiching a Pt counter electrode and a polyoxometalate photosensitizer sensitized photocathode. The electrolyte solution was then filled through the holes predrilled on the Pt electrode by applying vaccum. Afterward the holes were sealed with glass cover slide.

Characterization Methods

The UV-Vis spectra test were recorded on a Varian Cary 50 conc UV-Visible spectrophotometer in the range of 350-800nm. IR spectra were recorded using KBr pellets on a Bruker AXS TENSOR-27 FTIR spectrometer in the range of 4000−400 cm−1. TG curves were performed on a PerkinElmer TGA7 instrument at a heating rate of 10 °C/min from 25 °C to 600 °C. The diffuse reflectivity spectra were collected on a UV-2600 SHIMADZU UV−vis spectrophotometer in reflectance mode, which was measured from 220 nm to 850 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance. Cyclic voltammograms were recorded on a CHI601D Electrochemical Workstation (Shanghai Chenhua Instrument Corp., China) at room temperature, using a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag^+ reference electrode. 0.1 M $LiClO_4$ was used as the supporting electrolyte. X-ray spectroscopy (EDS) of the samples was obtained from FEI Quanta 200 F microscope operated at an accelerating voltage of 20 kV. A Keithley 2400 source meter and a Zolix Omni-300 monochromator equipped with a 500 W xenon lamp were used for photocurrent action spectrum measurements, with a wavelength sampling interval of 10 nm and a current sampling time of 2 s under the

full computer control. J−V characteristics and other photoelectrochemical experiments were performed on a CHI601D electrochemical workstation at room temperature equipped with the xenon lamp as the light source and an AM 1.5 solar filter.

Supplementary Physical and Chemical Characterizations

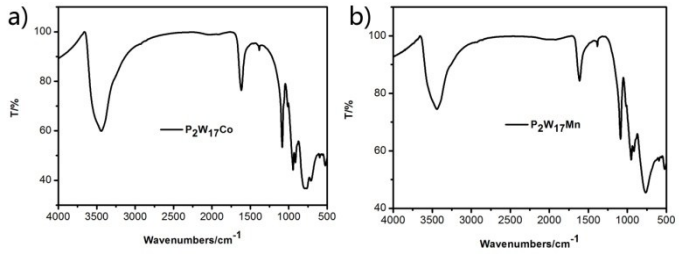

Figure. S1 IR spectra of $P_2W_{17}Co$(a) and $P_2W_{17}Mn$(b).

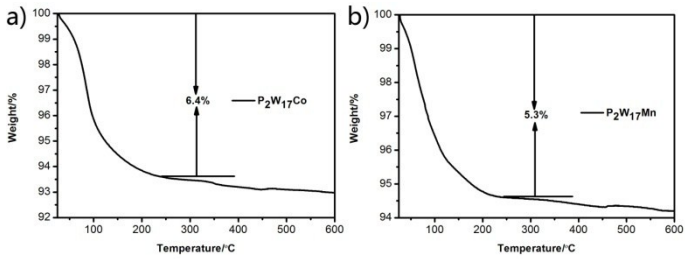

Figure. S2 TG analysis of $P_2W_{17}Co$(a) and $P_2W_{17}Mn$(b).

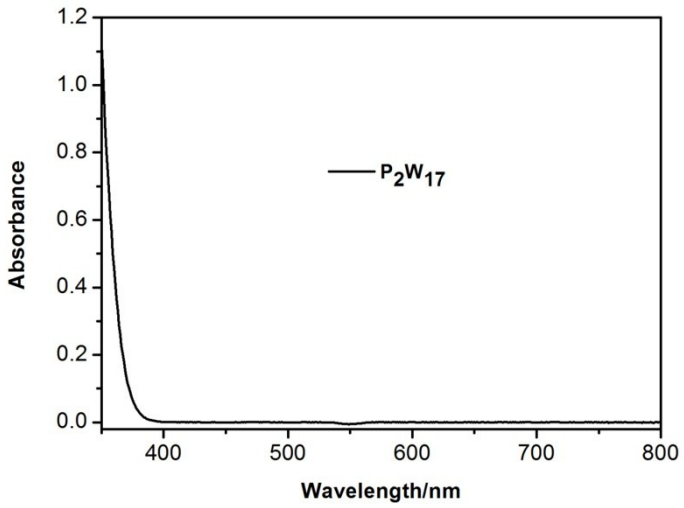

Fig. S3. the UV-vis spectrum of 1mM $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in DMSO.

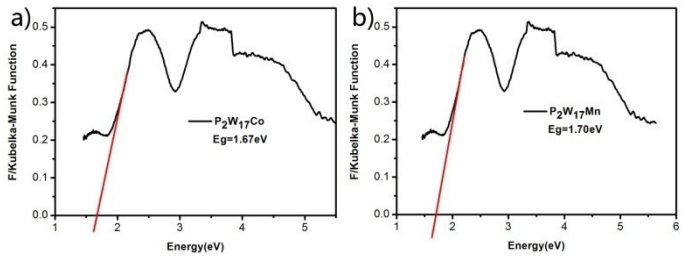

Figure. S4 Diffuse reflectivity spectra and plot of Kubelka–Munk function F against energy E of $P_2W_{17}Co$(a) and $P_2W_{17}Mn$(b).

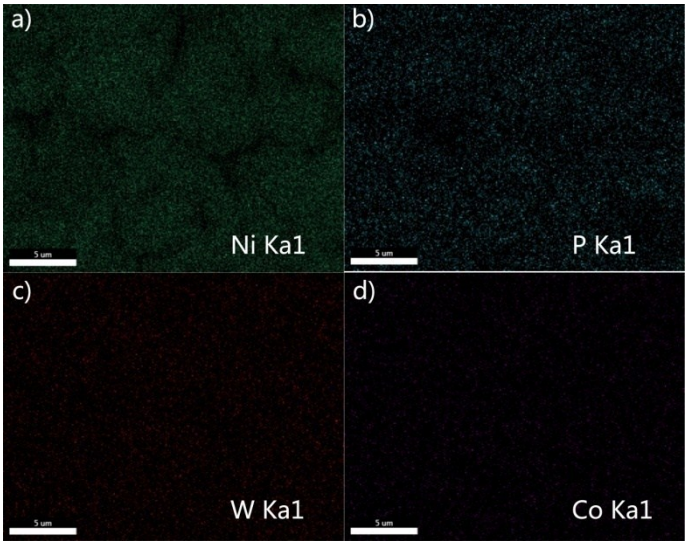

Figure. S5 Element mapping of $P_2W_{17}Co$ sensitived NiO electrode.

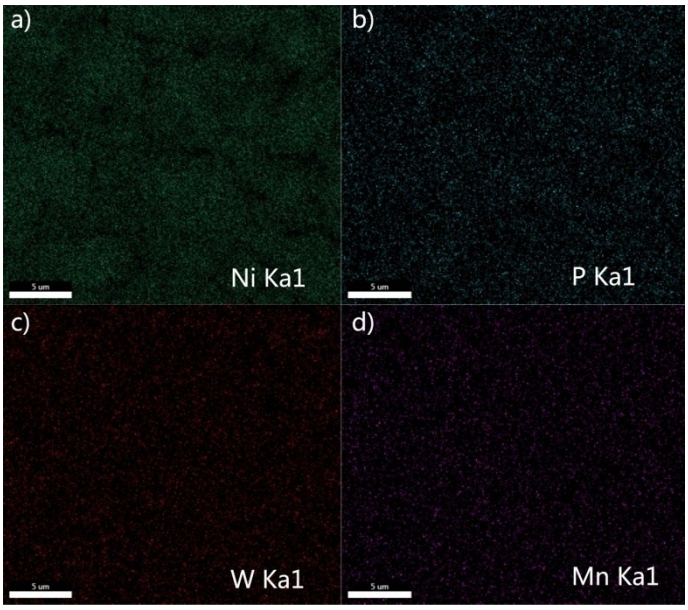

Figure. S6 Element mapping of $P_2W_{17}Mn$ sensitived NiO electrode.

Table. S1 Parameters of photovoltaic performance for different dyes measured under 100 mW/cm^2 simulated AM1.5G irradiation based on mesoporous NiO electrodes.

Dye	Electrolyte	V_{oc}(mV)	J_{sc}(mA/cm^2)	FF	PCE(%)	Reference
erythrosine B	I_3^-/I^-	82.8	0.232	0.27	0.0076	S2
C343	I_3^-/I^-	70	0.78	0.32	0.017	S3
P1		110	1.52	0.31	0.052	
P4	I_3^-/I^-	100	2.48	0.36	0.09	S4
$[Ru(dcb)_2(NMI\text{-}phen)](PF_6)_2$	I_3^-/I^-	95	0.16	0.36	0.006	S5
IrPhen	$Co(dtbpy)_3^{3+/2+}$	345	0.14	0.44	0.021	S6
IrDPQCN2		508	0.25	0.54	0.068	
IrBpystyryl		383	0.37	0.44	0.061	
PMI-6T-TPA	I_3^-/I^-	218	5.35	0.35	0.41	S7
O2	I_3^-/I^-	94	1.43	0.37	0.050	S8
O6		97	1.04	0.37	0.037	

O7		90	1.74	0.38	0.060	
O8	I_3^-/I^-	63	0.44	0.36	0.009	S8
O11		79	1.16	0.36	0.033	
O12		92	1.84	0.34	0.051	
O3	I_3^-/I^-	93	3.04	0.35	0.099	S10
O13		89	2.66	0.31	0.074	
O17		92	2.69	0.34	0.085	

Table. S2 Photovoltaic parameters of a batch of 9 devices measured under 100 mW/cm^2 simulated AM1.5G irradiation based on mesoporous NiO electrodes.

100%Sun	0.03MP_2W_{17}Co + 0.015MP_2W_{17}Mn		
	Cell-1	Cell-2	Cell-3
V_{oc}(mV)	102	100	102
J_{sc}(mA/cm^2)	1.51	1.51	1.49
FF	0.299	0.307	0.305
PCE(%)	0.0461	0.0464	0.0464
100%Sun	0.03M P_2W_{17}Co		
	Cell-1	Cell-2	Cell-3
Voc(mV)	100	103	102
J_{sc}(mA/cm^2)	1.3	1.25	1.49
FF	0.301	0.32	0.305
PCE(%)	0.0391	0.0412	0.0464
100%Sun	0.03M P_2W_{17}Mn		
	Cell-1	Cell-2	Cell-3
V_{oc}(mV)	87	82	84
J_{sc}(mA/cm^2)	1.21	1.279	1.268
FF	0.302	0.299	0.296
PCE(%)	0.0318	00314	0.0315

Table. S3 Parameters of photovoltaic performance for $P_2W_{17}Mn$ of different concentrations measured under 100 mW/cm^2 simulated AM1.5G irradiation based on mesoporous NiO electrodes.

$P_2W_{17}Mn$	V_{oc}(mV)	J_{sc}(mA/cm^2)	FF	PCE(%)
0.015 M	83	1.144	0.297	0.0282
0.020 M	84	1.188	0.290	0.0289
0.025 M	85	1.201	0.289	0.0295
0.030 M	84	1.268	0.296	0.0315
0.035 M	83	1.255	0.292	0.304
0.040 M	85	1.187	0.298	0.0300

Table. S4 Optomization of concentrations of $P_2W_{17}Co$ and $P_2W_{17}Mn$. Photovoltaic parameters of a batch of 6 devices measured under 100 mW/cm^2 simulated AM1.5G irradiation based on mesoporous NiO electrodes.

$P_2W_{17}Co$ + $P_2W_{17}Mn$	V_{oc}(mV)	J_{sc}(mA/cm^2)	FF	PCE(%)
0.03 M + 0.005 M	100	1.31	0.302	0.0396
0.03 M + 0.010 M	102	1.38	0.299	0.0421
0.03 M + 0.015 M	101	1.48	0.31	0.0463
0.03 M + 0.020 M	98	1.478	0.304	0.044
0.03 M + 0.025 M	95	1.503	0.301	0.0428
0.03 M + 0.030 M	90	1.51	0.297	0.0404

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