Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for:

Aqueous p-type dye-sensitized solar cells based on the tris(1,2-diaminoethane) cobalt(II)/(III) redox mediator

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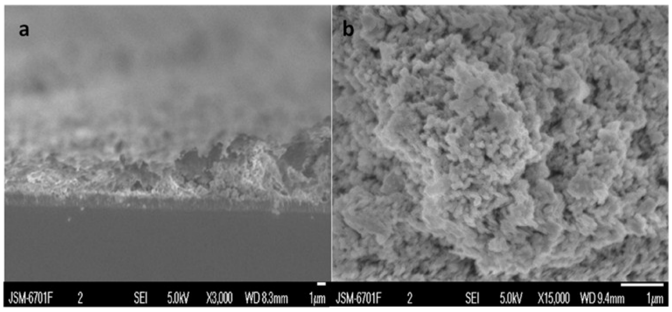

Figure S1 Scanning electron microscope of mesoporous NiO film on FTO substrate. a) Cross-sectional image, b) top-view image.

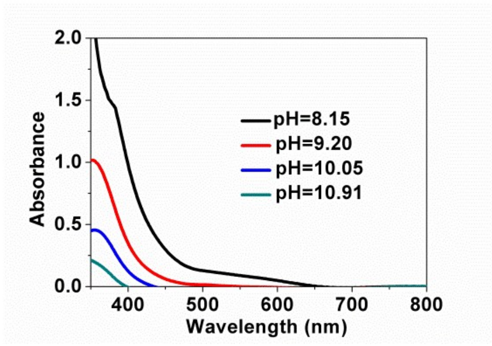

Figure S2 UV-Visible spectra of aqueous electrolytes with different pHs. The electrolytes contained 0.6 M $[Co(en)_3](BF_4)_2$, 0.07 M $[Co(en)_3](BF_4)_3$, 0.9 M $LiBF_4$ and 0.3 M NMBI in deionized water, where either boric acid or 1,2-diaminoethane were used to adjust the electrolyte pHs. An aqueous solution containing 0.9 M $LiBF_4$ and 0.3 M NMBI was used as blank.

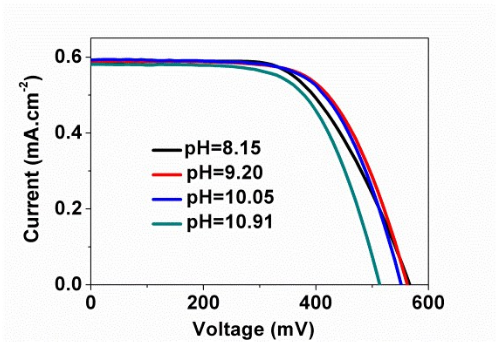

Figure S3 J-V curves for p-type DSCs based on $[Co(en)_3]^{2+/3+}$ electrolytes with different pHs at 0.1 sun light intensity illumination.

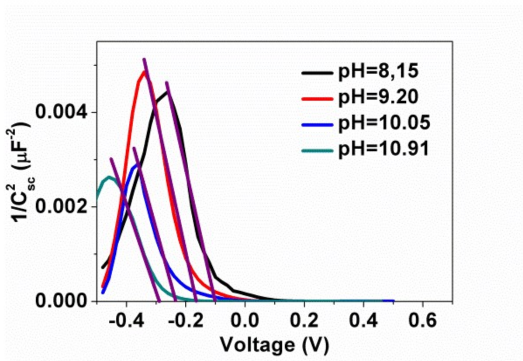

Figure S4 Mott-Schottky behavior of NiO contacting with different pH electrolytes. The experiment was carried out by a three-electrodes setup. A 7×7 mm NiO film was used for working electrode. Platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. Boric acid and 1,2-diaminoethane were used to adjust the pH of the electrolytes. The scan range was from -0.5 V to 0.5 V vs Ag/AgCl and the frequency was chosen at 1 Hz for figure plotting. The linear fitting results were extrapolated to $1/(C_{SC})^2 = 0$.

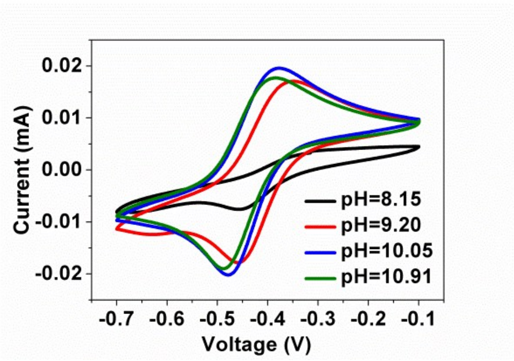

Figure S5 Cyclic voltammetry of $[Co(en)_3]^{2+/3+}$ redox mediator in different pH electrolytes. The measurement was conducted at a 20 mV s^{-1} scan rate in the range of -0.7 to -0.1 V vs Ag/AgCl.The aqueous electrolyte solution contained 6 mM $[Co(en)_3](BF_4)_2$, 0.7 mM $[Co(en)_3](BF_4)_3$ and 0.1 M potassium chloride, in water, where boric acid and extra 1,2-diaminoethane were used to adjust electrolyte pHs.

Table S1 Optimization of $[Co(en)_3](BF_4)_2$ concentration in aqueous electrolytes used in p-type DSCs at a pHs of 8.15. Other components in electrolyte are: 0.10 M $[Co(en)_3](BF_4)_3$, 0.10 M NMBI, 0.50 M $LiBF_4$ in water. The NiO film thickness is 2.4 µm. Device performance data is the average of at least three devices. Photovoltaic parameters were recorded under light intensities of 1000 mW cm^{-2}.

$[Co(en)_3]$ $(BF_4)_2$ (M)	V_{OC} (mV)	J_{SC} (mAcm^{-2})	*FF*	η (%)
0.2	584±3	3.52±0.02	0.29±0.01	0.60±0.10
0.4	572±5	3.81±0.01	0.34±0.01	0.73±0.06
0.6	564±4	4.44±0.01	0.40±0.01	1.01±0.05
0.8	553±6	4.52±0.01	0.39±0.01	0.97±0.07

Table S2 Optimization of $[Co(en)_3](BF_4)_3$ concentration in aqueous electrolytes used in p-type DSCs at a pH of 8.15. Other components in electrolyte are: 0.60 M $[Co(en)_3](BF_4)_2$, 0.10 M NMBI, 0.70 M $LiBF_4$ in water (NiO film thickness is 2.4 µm; photovoltaic parameters recorded at 1000 mW cm^{-2}; data averaged for at least three devices).

$[Co(en)_3]$ $(BF_4)_3$ (M)	V_{OC} (mV)	J_{SC} (mAcm^{-2})	*FF*	η (%)
0.07	582±8	5.90±0.04	0.41±0.01	1.42±0.17
0.27	600±6	4.85±0.02	0.41±0.01	1.19±0.13
0.47	615±7	4.72±0.05	0.42±0.01	1.22±0.11
0.67	595±5	4.22±0.02	0.45±0.01	1.13±0.10

Table S3 Optimization of NMBI concentration in aqueous electrolyte used in p-type DSCs at a pH of 8.15. Other components in electrolyte are: 0.2 M $[Co(en)_3](BF_4)_2$, 0.10 M $[Co(en)_3](BF_4)_3$, 0.30 M $LiBF_4$ in water (NiO film thickness is 2.4 µm; photovoltaic parameters recorded at 1000 mW cm^{-2}; data averaged for at least three devices).

NMBI (M)	V_{OC} (mV)	J_{SC} (mAcm^{-2})	*FF*	η (%)
0	362±5	0.67±0.01	0.47±0.01	0.11±0.03
0.1	696±8	2.79±0.04	0.23±0.01	0.45±0.09
0.3	684±6	3.64±0.07	0.23±0.01	0.57±0.17
0.5	672±7	1.68±0.01	0.25±0.01	0.28±0.07

Table S4 Optimization of $LiBF_4$ concentration in aqueous electrolyte for p-type DSCs at a pH of 8.15. Other components in electrolyte are: 0.60 M $[Co(en)_3]$ $(BF_4)_2$, 0.10 M $[Co(en)_3]$ $(BF_4)_3$, 0.30 M NMBI in water (NiO film thickness is 2.4 µm; photovoltaic parameters recorded at 1000 mW cm^{-2}; data averaged for at least three devices).

$LiBF_4$ (M)	V_{OC} (mV)	J_{SC} (mAcm^{-2})	*FF*	η (%)
0	531±2	0.43±0.01	0.59±0.01	0.14±0.02
0.5	553±7	3.35±0.02	0.41±0.01	0.75±0.16
0.7	583±10	4.79±0.08	0.41±0.01	1.14±0.20
0.9	609±8	6.02±0.05	0.40±0.01	1.46±0.17
1.2	581±8	6.14±0.10	0.40±0.01	1.42±0.13

Table S5 Optimization of NiO film thickness for aqueous p-type DSCs assembled using an electrolyte with pH of 8.15. The components in electrolyte are: 0.20 M $[Co(en)_3](BF_4)_2$, 0.10 M $[Co(en)_3]$ $(BF_4)_3$, 0.10 M NMBI, 0.30 M $LiBF_4$ in water (NiO film thickness is 2.4 µm; photovoltaic parameters recorded at 1000 mW cm^{-2}; data averaged for at least three devices).

Thickness (µm)	V_{OC} (mV)	J_{SC}(mAcm^{-2})	*FF*	η (%)
0.8	692±10	2.81±0.05	0.25±0.01	0.49±0.20
1.6	689±8	4.13±0.07	0.27±0.01	0.77±0.19
2.4	682±7	4.30±0.05	0.30±0.01	0.89±0.17
3.2	661±6	4.22±0.04	0.29±0.01	0.80±0.10
4.0	651±7	4.12±0.04	0.24±0.01	0.65±0.11

Table S6 Valence band potentials (E_{VB}) and acceptor-state densities (N_A) of NiO in contact with different pH electrolytes. Data were fitted and calculated from Mott-Schottky curves in **Figure S4** using equation (1) given in main text.

pH	E_{VB}(V vs NHE) extrapolated	N_A($\times 10^{19}$cm^{-3})
8.15	0.30±0.04	2.23±0.06
9.20	0.24±0.02	2.05±0.13
10.05	0.17±0.06	1.91±0.08
10.91	0.11±0.04	1.82±0.04

Table S7 Parameters obtained by CV measurements for the redox mediators with different pH electrolytes (vs NHE).

pH	E_{Ox} (V)	E_{Red} (V)	E_{Mid} (V)	ΔE (= E_{Ox}– E_{Red}) (V)	I_{Ox}/I_{Red}
8.15	-0.14±0.04	-0.25±0.03	-0.19±0.06	0.12±0.03	0.44±0.03
9.20	-0.16±0.06	-0.26±0.03	-0.21±0.05	0.10±0.05	1.03±0.06
10.05	-0.19±0.03	-0.27±0.02	-0.23±0.03	0.08±0.02	0.99±0.02
10.91	-0.19±0.03	-0.28±0.04	-0.24±0.04	0.09±0.03	0.97±0.04