

Electronic Supplementary Information (ESI)
for
Highly water-soluble three-redox state organic dyes as
bifunctional analytes

Javier Carretero-González,^{‡a*} Elizabeth Castillo-Martínez,^{‡a} and Michel Armand^a

^aCIC EnergiGUNE, Alava Technology Park, C/ Albert Einstein 48 Ed. CIC, Minaño,

Álava 01510, Spain

*E-mail: jc966@cam.ac.uk, jabenzo@hotmail.com

[‡] Present address: Department of Chemistry, University of Cambridge,

Lensfield Road, Cambridge CB2 1EW, UK

This file includes:

Additional Methods:

Infrared Spectroscopy.

Raman Spectroscopy.

X-Ray Diffraction.

Thermogravimetric Analysis.

Nuclear Magnetic Resonance

Supplemental Figures:

Figure S1: Cyclic voltammogram of Naphtazarin.

Figure S2: Cyclic voltammograms of Indigo and Indigo Carmine and protonated Indigo Carmine in both acidic and basic aqueous based electrolyte.

Figure S3: Cyclic Voltammogram of bis-quinones in basic and neutral pH.

Figure S4: X-Ray diffraction of the three families of organic dye's derivatives studied here.

Figure S5: IR and Raman characterization of Quinizarin and Quinizarin-SO₃⁻Na.

Figure S6: IR characterization of the three families of organic dyes studied along the present work.

Figure S7: Thermogravimetric analysis in air and argon atmosphere.

Figure S8: Electrochemical properties of protonated Indigo Carmine in acidic and basic aqueous based electrolyte.

Figure S9: Cyclic voltammogram of Quinizarin derivatives.

Figure S10: Cyclic voltammogram of Alizarin derivatives.

Figure S11: ¹H NMR spectroscopy of Indigo Carmine and its oxidized form.

Figure S12: ¹³C NMR spectroscopy of Indigo Carmine and its oxidized form.

Figure S13: ¹H and ¹³C NMR spectroscopy of Indigo Carmine and its reduced form.

Figure S14: ¹H and ¹³C NMR spectroscopy of Alizarin S. Red and its oxidized and reduced forms.

Supplemental Tables:

Table S1: Content of water molecules on each organic dye's derivatives.

Table S2: Solubility results.

Additional Methods.

Infrared Spectroscopy. ATR-FTIR spectra were recorded on Vertex 70 spectrometer (Bruker) in the range of wavelength of 4000-400 cm^{-1} .

Raman Spectroscopy. Raman spectra were recorded with a Renishaw spectrometer (Nanonics multiview 2000) operating with an excitation wavelength of 532 nm. The spectrum was acquired after 20 seconds of exposition time of the laser beam to the sample.

X-Ray Diffraction. Powder X-ray diffraction of dried powdered samples was collected on a Bruker Advance D8 instrument with copper radiation ($\text{CuK}\alpha_{1,2}$, $\lambda=1.54056 \text{ \AA}$) in the 2θ range from 4° to 80° with a step size of 0.02.

Thermogravimetric Analysis. The measurements were performed on a Netzsch STA 449 F3 Jupiter analyzer. Experiments were performed in the temperature range from 30°C to 900°C using Ar (60 ml min^{-1}) or Air (60 ml min^{-1}) atmosphere and a temperature step of 5°C min^{-1} .

Nuclear Magnetic Resonance. Liquid Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) were recorder using a Bruker DCH Cryoprobe (500 MHz) at 25°C . Both proton and carbon chemical shifts were expressed in parts per million (ppm).

Supplemental Figures:

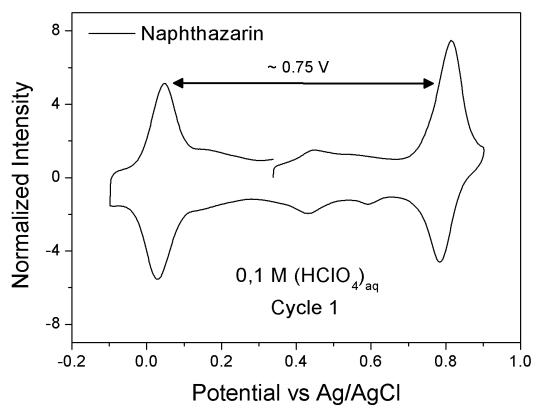


Figure S1. Cyclic voltammogram of 5,8-dihydroxy-1,4-naphthoquinone (Naphthazarin) in 0.1M HClO₄ in the -0.1 V to + 0.9 V vs Ag/AgCl range. (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

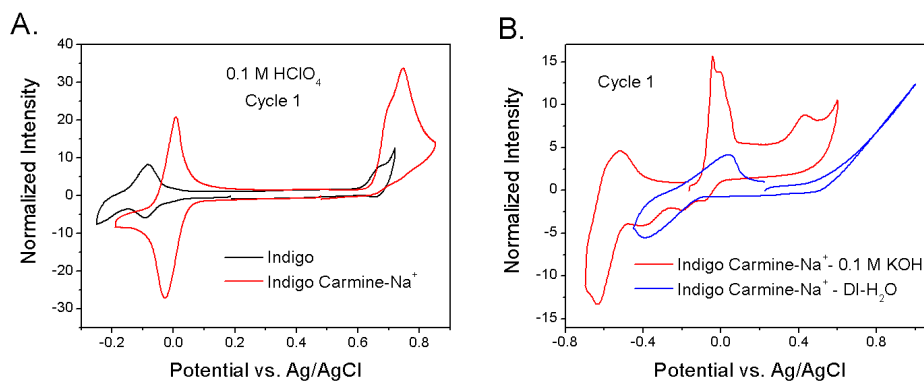


Figure S2. Cyclic voltammograms (1st cycle) of (A) Indigo and Indigo Carmine in 0.1 M HClO₄; (B) Indigo Carmine in 0.1M KOH (red line) and in DI-H₂O (blue line). (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

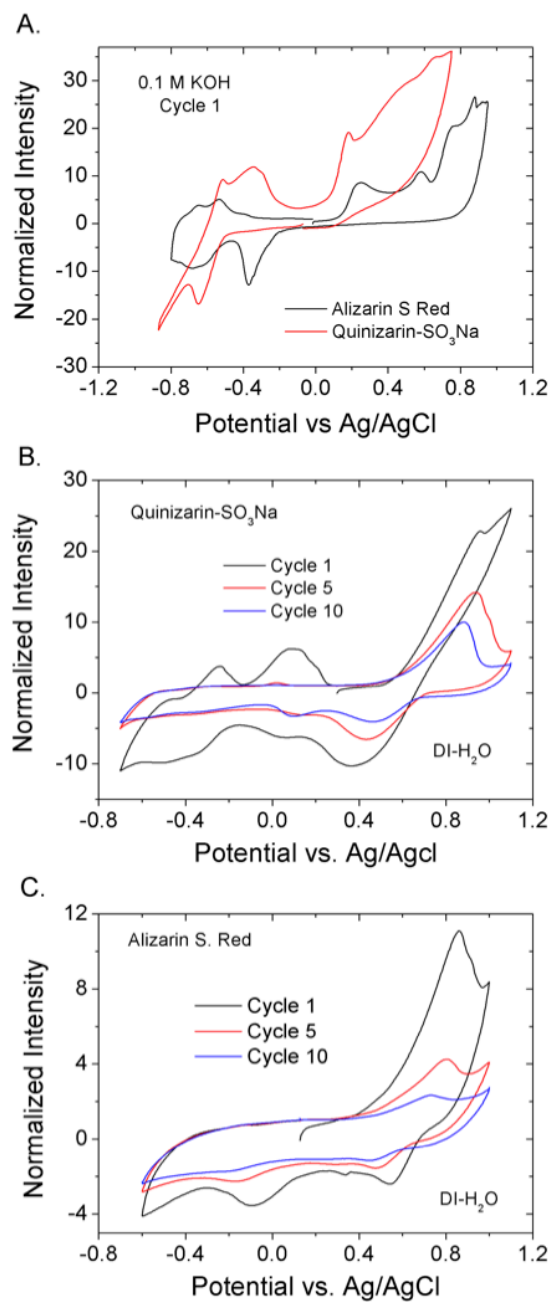


Figure S3. Cyclic voltammograms of bis-quinones in basic and neutral pH. (A) First cycle for Alizarin S. Red and Quinizarine-SO₃Na in 0.1M KOH. (B) Cycles 1, 5 and 10 for Quinizarine-SO₃-Na in DI-H₂O. (C), Cycles 1, 5 and 10 for Alizarine S Red in DI-H₂O. (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

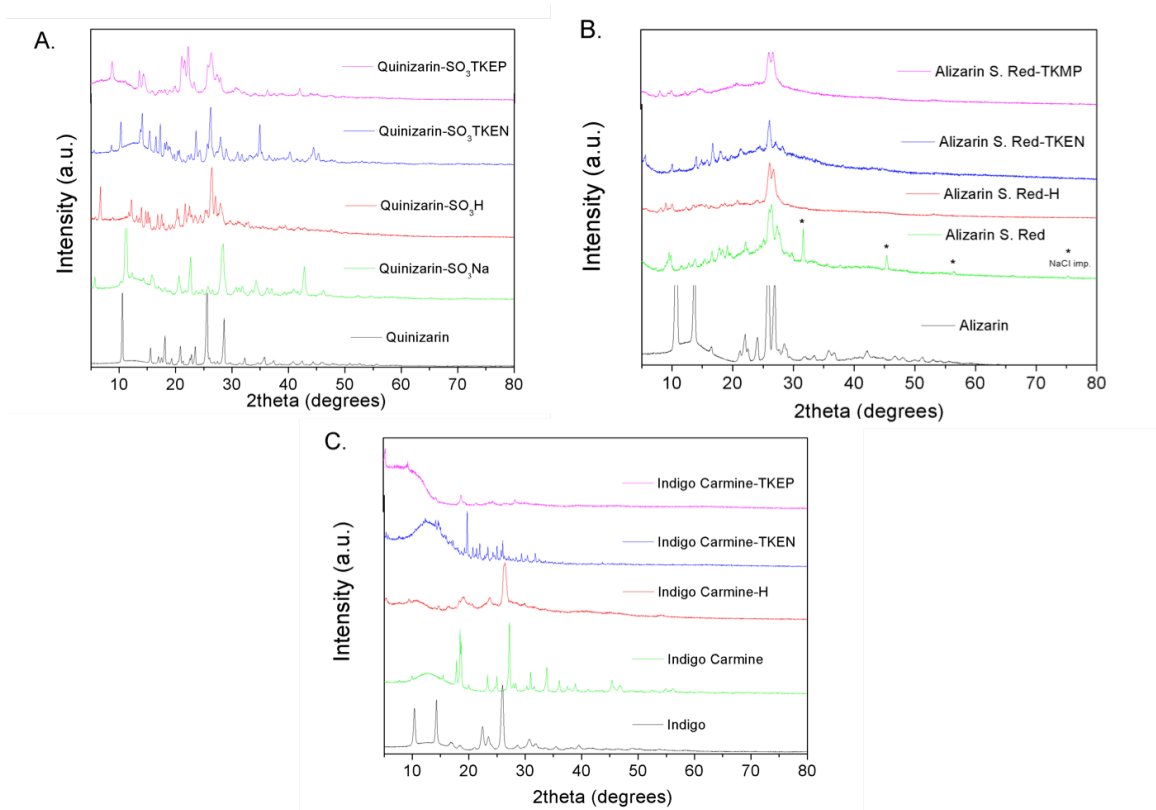


Figure S4. Powder X-Ray diffraction patterns for the three families of dye's derivatives studied here showing that upon sulfonation and cationic exchange the salts present different crystal structures. (A) Quinizarin, (B) Alizarin, and (C) Indigo derivatives.

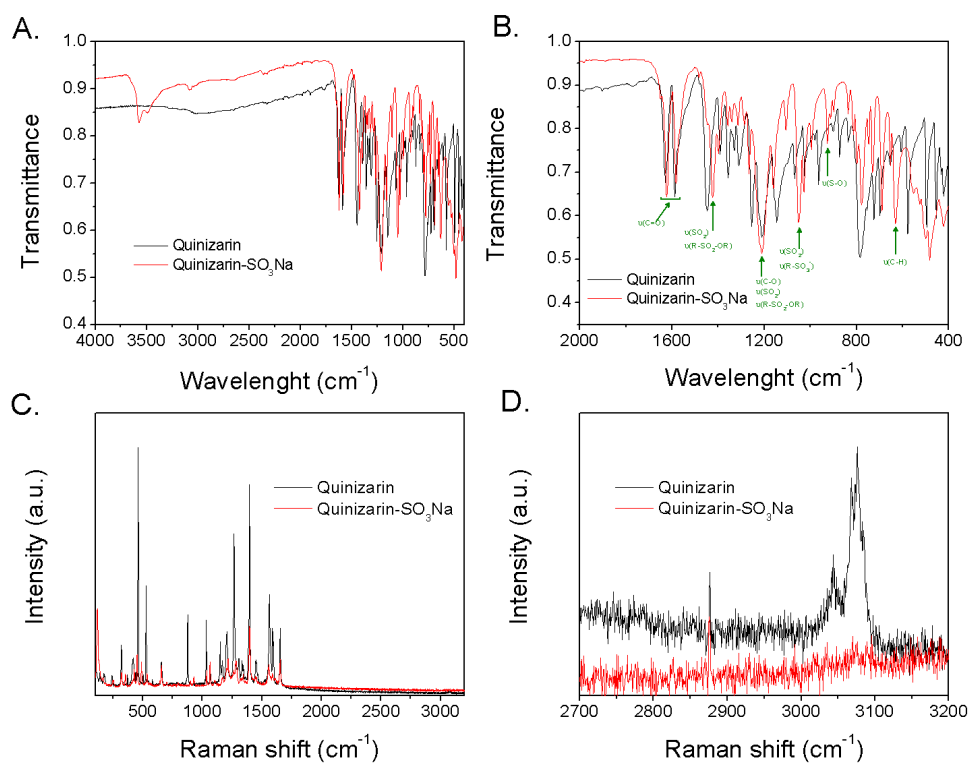


Figure S5. (A-B) IR and (C-D) Raman spectra of commercial Quinizarin and as prepared Quinizarin-SO₃Na analytes showing new vibrations due to the sulphonate groups.

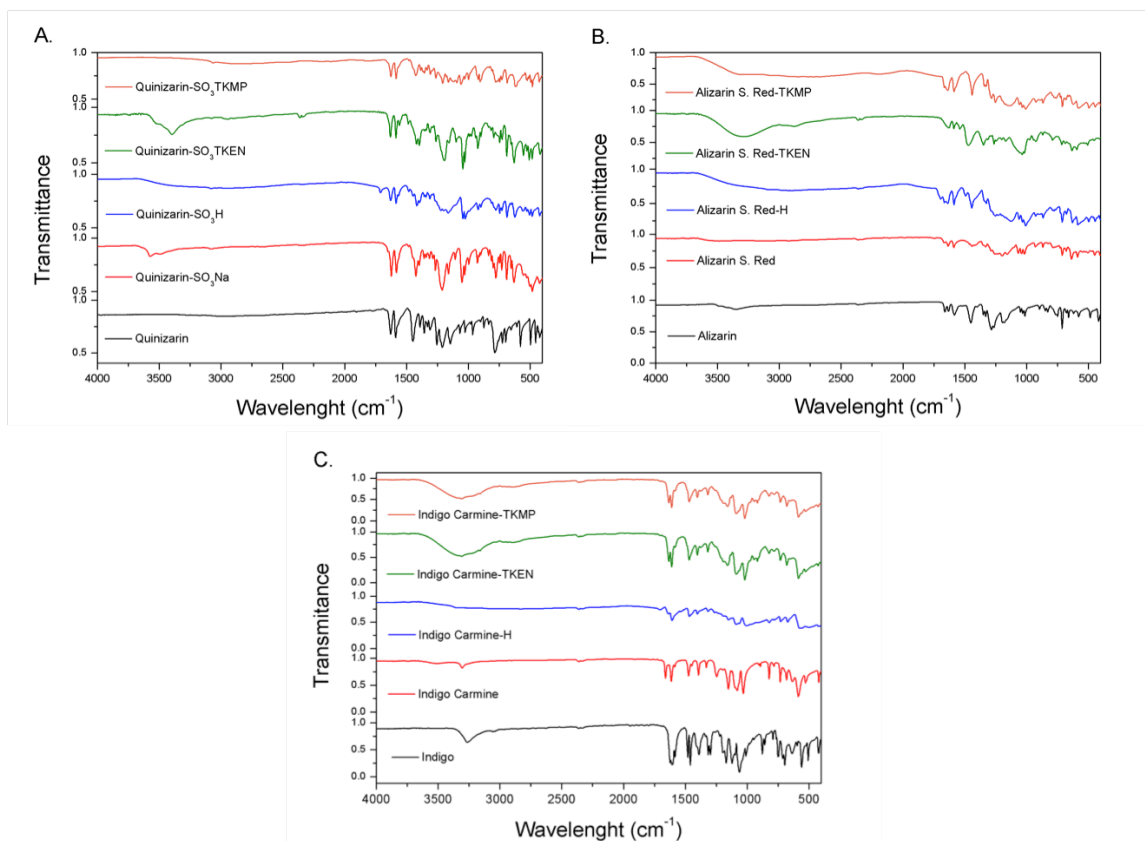


Figure S6. IR characterization of the three families of organic analytes studied along the present work. (A) Quinizarin based (B) Alizarin and (C) Indigo derivatives.

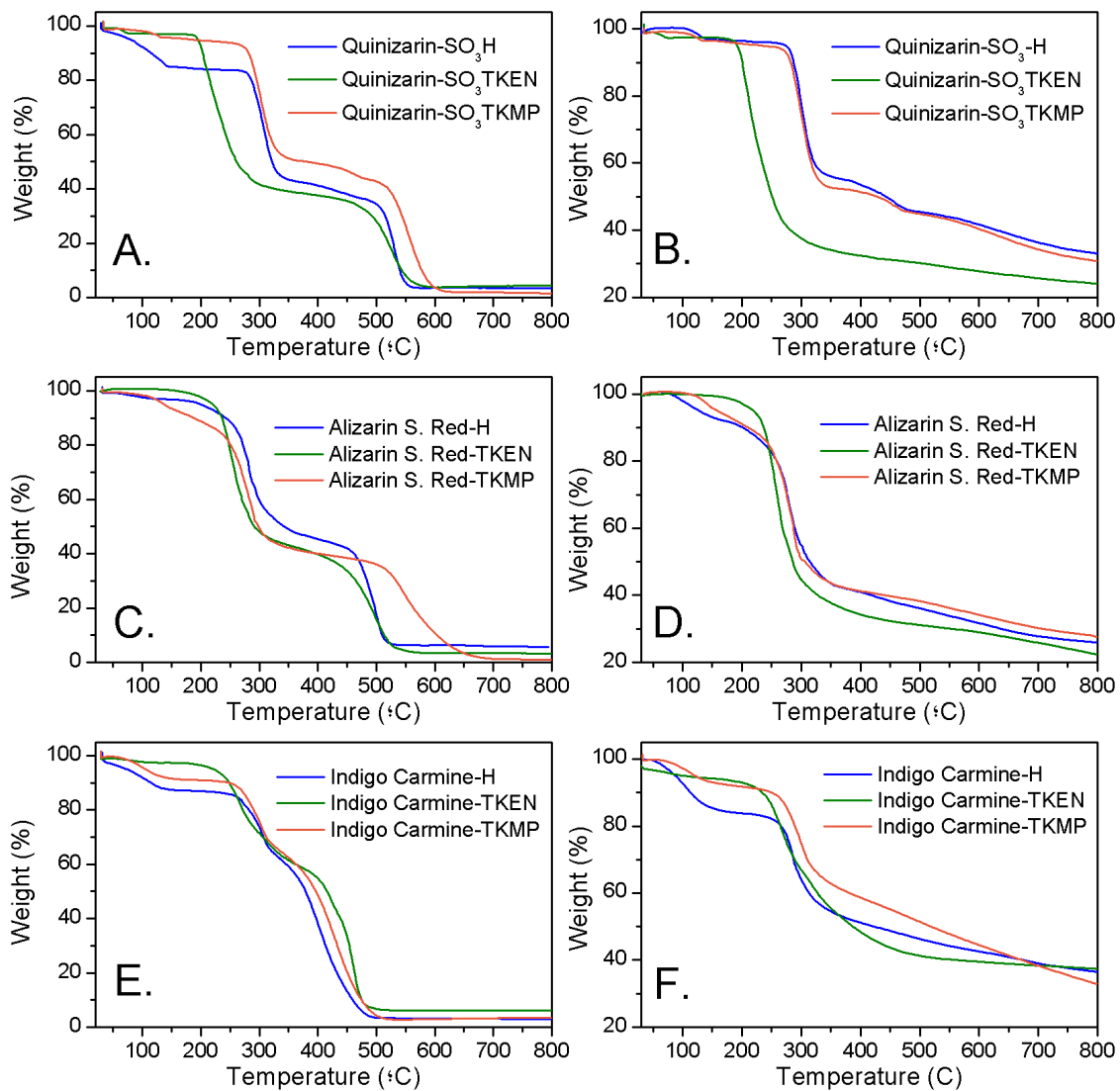


Figure S7. Thermogravimetric analysis of three salts of three water-soluble organic analytes studied here under Air (A-C-E) and Argon (B-D-F) atmosphere.

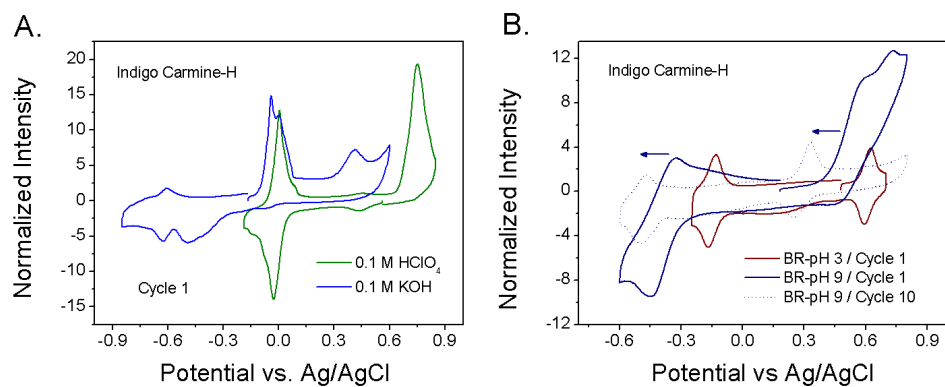


Figure S8. (A) Electrochemical properties of protonated Indigo Carmine in acidic and basic aqueous based electrolyte; (B) protonated Indigo Carmine in BR pH 3 and 9 (cycles 1 and 10); (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

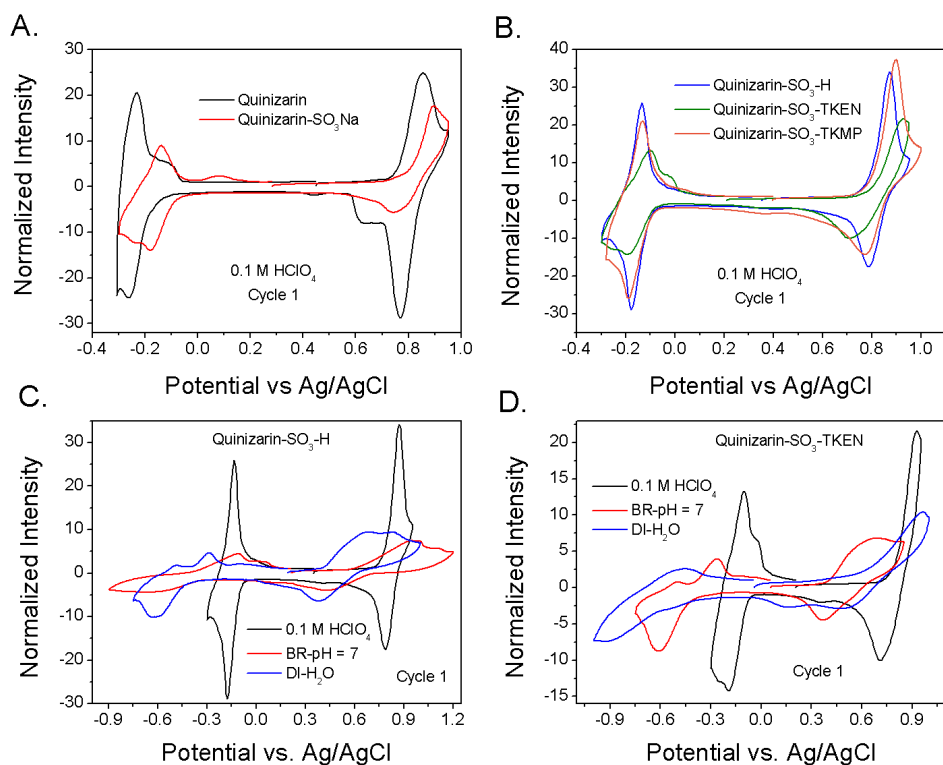


Figure S9. Cyclic Voltammogram of Quinizarin derivatives. (A) Quinizarin and sulphonated quinizarin in 0.1M HClO₄; (B) Sulphonated quinizarin with Na exchanged by H⁺, TKEN⁺ and TKMP⁺ in 0.1M HClO₄; (C) H⁺ substituted sulphonated quinizarine in 0.1M HClO₄, BR at pH=7 and D.I. water; (D) TKEN substituted sulphonated quinizarine in 0.1M HClO₄, BR at pH=7 and D.I. water. (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

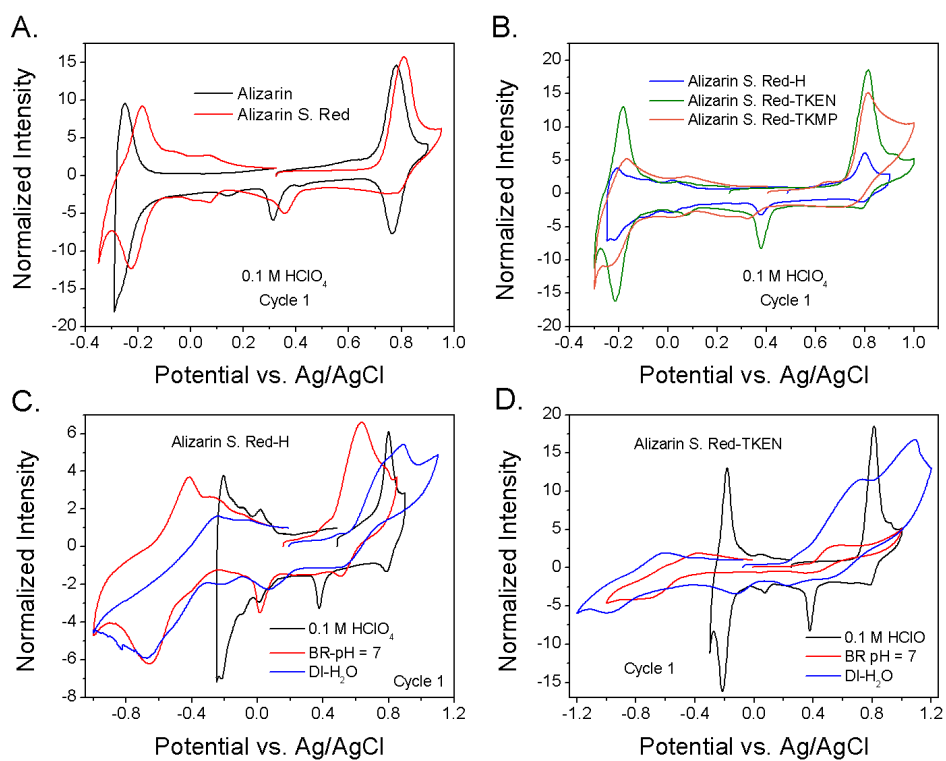


Figure S10. Cyclic voltammogram of Alizarin derivatives. (A) Alizarin and sulphonated alizarin (Aliz S Red) in 0.1M HClO₄; (B) Alizarine S Red with Na exchanged by H⁺, TKEN⁺ and TKMP⁺ in 0.1M HClO₄; (C) H⁺ substituted Alizarine S Red in 0.1M HClO₄, BR at pH=7 and D.I. water; (D) TKEN substituted Alizarine S Red in 0.1M HClO₄, BR at pH=7 and D.I. water. (Pt was used as counter electrode and Ag/AgCl as reference electrode; Scan rate = 200 mV s⁻¹).

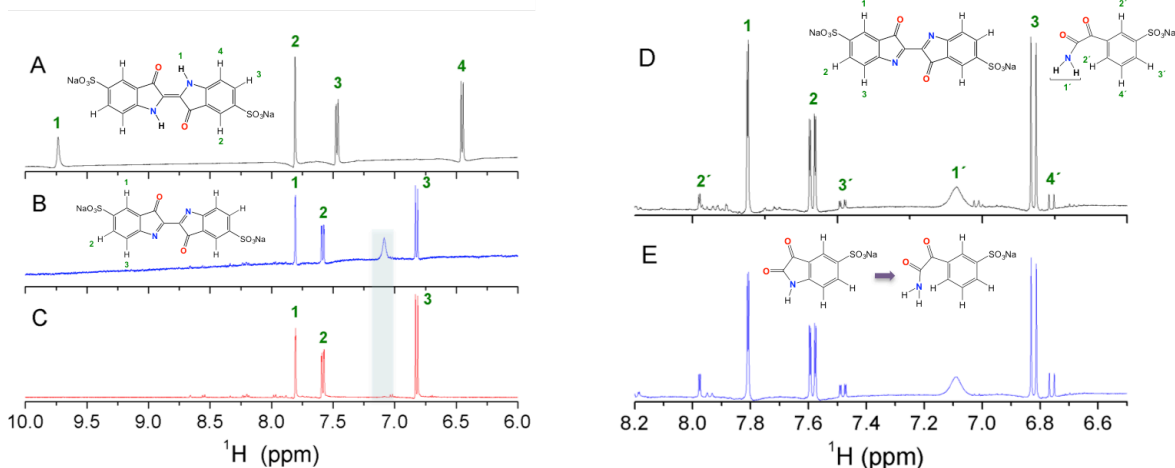


Figure S11. ^1H NMR spectra of pristine Indigo Carmine and Indigo Carmine after chemical oxidation by using PbO_2 in deoxygenated and deionized water ($\text{DI-H}_2\text{O}$). (A) ^1H NMR spectrum of Indigo Carmine in deionized water; (B) ^1H NMR spectrum of the oxidized form of Indigo Carmine at room temperature exhibiting an extra broad resonance at ~ 7.1 ppm (shadow blue area). (C) 1D NOESY spectrum showing the suppression of those proton nuclei that are easily exchangeable with the $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixture. (D) Highly resolved (higher number of scans than the spectrum shown in Figure S11C) ^1H NMR spectrum of the oxidized form of Indigo Carmine evidencing resonances corresponding to the Isatin derivative produced by peroxidative cleavage of the carbon-carbon double bond in the Indigo Carmine molecule. (E) ^1H NMR spectrum corresponding to the oxidation reaction performed at 50°C .

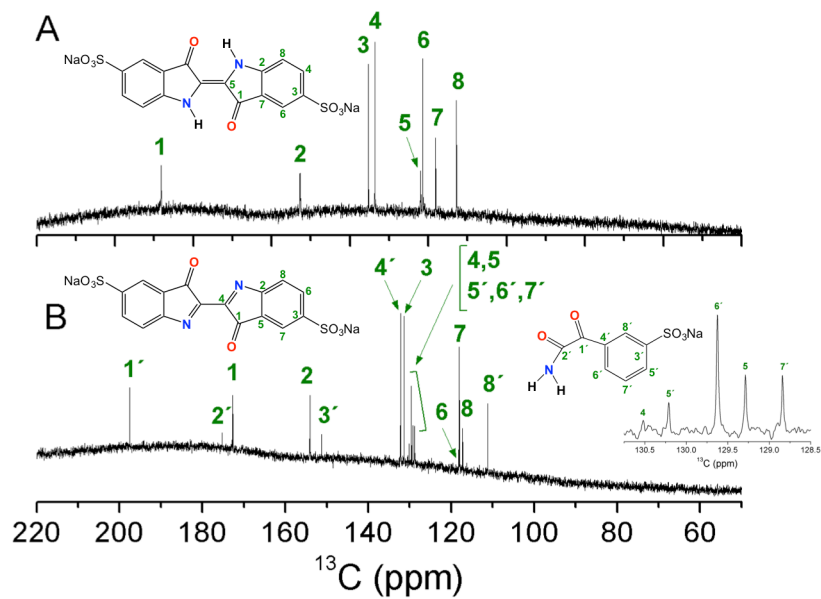


Figure S12. ^{13}C NMR spectra of (A) pristine Indigo Carmine and (B) Indigo Carmine after chemical oxidation at room temperature by using PbO_2 in deoxygenated and deionized water ($\text{DI-H}_2\text{O}$).

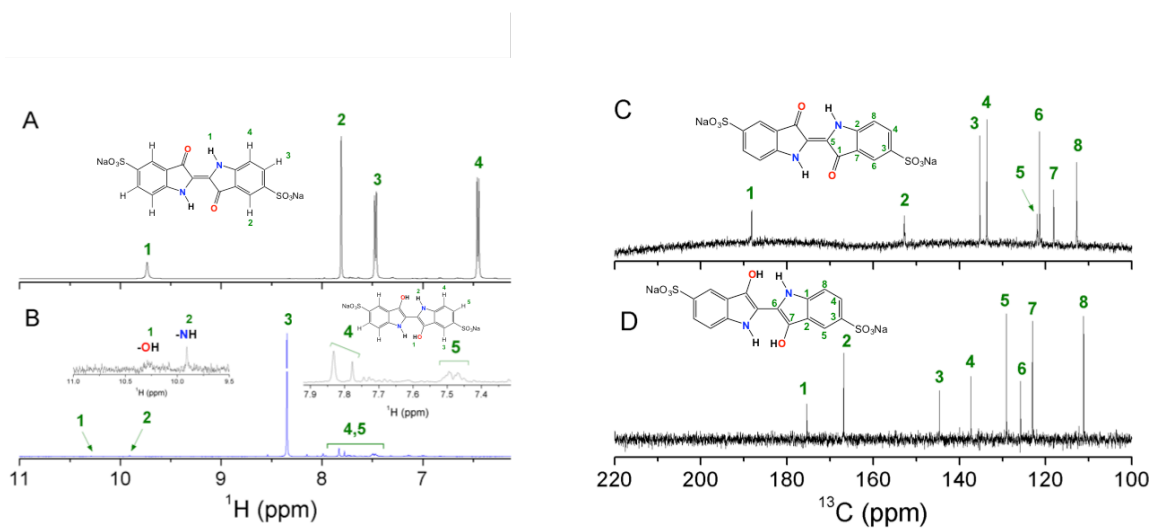


Figure S13. ^1H (A)-(B) and ^{13}C (C)-(D) NMR spectra of pristine Indigo Carmine and Indigo Carmine after chemical reduction at room temperature by using $\text{Na}_2\text{S}_2\text{O}_4$ in deoxygenated and deionized water (DI- H_2O).

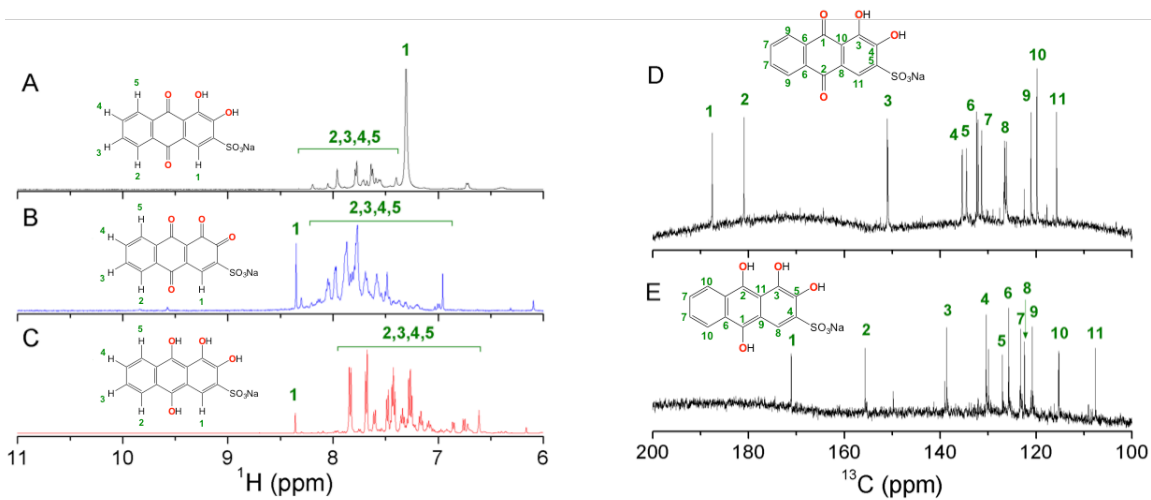


Figure S14. ^1H NMR spectra of (A) pristine Alizarin S. Red, (B) Alizarin S. Red chemically oxidized with PbO_2 and (C) Alizarin S. Red chemically reduced with $\text{Na}_2\text{S}_2\text{O}_4$. ^{13}C NMR spectra of (D) pristine Alizarin S. Red and (E) Alizarin S. red

chemically reduced. All the chemical reactions were carried out in deoxygenated and deionized water (DI-H₂O) at room temperature.

Supplemental Tables:

Table S1. Content of water molecules on each analyte derivatives as deduced from thermogravimetric analysis.

Quinizarin	Alizarin	Indigo
Q-H. 3.2 H ₂ O	A-H. 0.6 H ₂ O	I-H. 3.4 H ₂ O
Q-TKEN. 0.89 H ₂ O	A-TKEN. - H ₂ O	I-TKEN. 0.86 H ₂ O
Q-TKMP. 1.2 H ₂ O	A-TKMP. 1.8 H ₂ O	I-TKMP. 3.7 H ₂ O

Table S2. Solubility by adding incremental amounts of a known volume of solvent to a known weight of dye until dissolution.

Indigo derivatives	H ₂ O						R(OH) ₂ +NaOH pH=7						BR pH=9						BR pH=7						BR pH=3						0.1 M HClO ₄					
	MW g/mol	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)							
Indigo	262.26					30	0.114	825	<0.139	30.5	0.116	1425	<0.082	30	0.114	1425	<0.08	30.8	0.117	2000	<0.059															
Indigo Carbimide	466.35					29.6	0.063	500	<0.127	33	0.070	600	<0.118	30	0.043	600	<0.10	32.4	0.069	500	<0.139	48.2	0.103	775	<0.133											
Indigo Carbin-3H	422.36	30.8	0.072	125	0.583	27.2	0.064	171	0.375	27.5	0.065	173	0.375	27	0.063	170	0.37	32.4	0.076	204	0.375	64.3	0.152	200	0.761											
Indicarm- TKEN	780.35	18.1	0.023	30.3	0.766	15.6	0.02	26.1	0.766	22.7	0.029	38	0.766	22.5	0.028	37	0.765	21.6	0.027	36.1	0.765	25.5	0.032	45	0.726											
Indicarm- TKMP	730.35	28.8	0.039	125	<0.315									28	0.038	125	0.307					34.6	0.047	125	0.379											

Table S2. Solubility by adding incremental amounts of a known volume of solvent to a known weight of dye until dissolution.

Quinizarin derivatives	H ₂ O						R(OH) ₂ +NaOH pH=7						BR pH=9						BR pH=7						BR pH=3						0.1 M HClO ₄					
	MW g/mol	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)							
Quinizarin	240.21																																			
Quinizarin- SO ₂ Na	342					25.1	0.073	600	<0.122	25.2	0.073	875	<0.094	25.2	0.073	800	<0.092	25	0.073	1025	<0.071	27.5	0.080	650	<0.123											
Quinizarin- SO ₂ H	320					20.8	0.065	400	<0.163	21.9	0.068	850	<0.081	22.2	0.069	700	<0.099	21.4	0.066	950	<0.070	26.4	0.082	1700	<0.048											
Quinizarin- SO ₂ TKEN	513					20.6	0.040	200	<0.020	26.1	0.051	450	<0.113	21.1	0.041	400	<0.103	25	0.048	500	<0.097	22	0.042	800	<0.053											
Quinizarin- SO ₂ TKMP	474.26	28.8	0.0607	350	<0.174									27.6	0.0582	300	<0.194					30.1	0.063	300	<0.211											

Alizarin derivatives	H ₂ O						R(OH) ₂ +NaOH pH=7						BR pH=9						BR pH=7						BR pH=3						0.1 M HClO ₄					
	MW g/mol	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)	mass (mg)	n (mmol)	V (μl)	M (mol/l)							
Alizarin	240.21	30.5	0.127	2000	<0.063	35.1	0.1461	2000	<0.073	25	0.104	2000	<0.052	24.8	0.103	2000	<0.052	17.8	0.074	2000	<0.037	53.3	0.221	2000	<0.110											
Alizarin S-Red	342	36.5	0.106	600	<0.178	25.3	0.074	1600	0.046	21.4	0.062	900	<0.07	34.9	0.102	1000	<0.102	25.1	0.073	1400	<0.052	44.8	0.131	600	<0.218											
Alizarin S-Red- H	320	32.9	0.102	50	2.056	30.4	0.095	50	1.9	22.1	0.069	50	1.381	30	0.093	50	1.875	32.3	0.101	50	2.019	26.5	0.082	50	1.655											
Alizarin S-Red- TKEN	513	17.4	0.033	85	0.399	25.3	0.049	150	0.329	8.8	0.017	700	<0.025	23.6	0.046	700	<0.066	26.8	0.052	150	<0.348	24.5	0.047	120	0.398											
Alizarin S-Red- TKMP	474.26	26.3	0.055	50	1.109									25.5	0.053	100	0.538					39.4	0.083	50	1.661											

