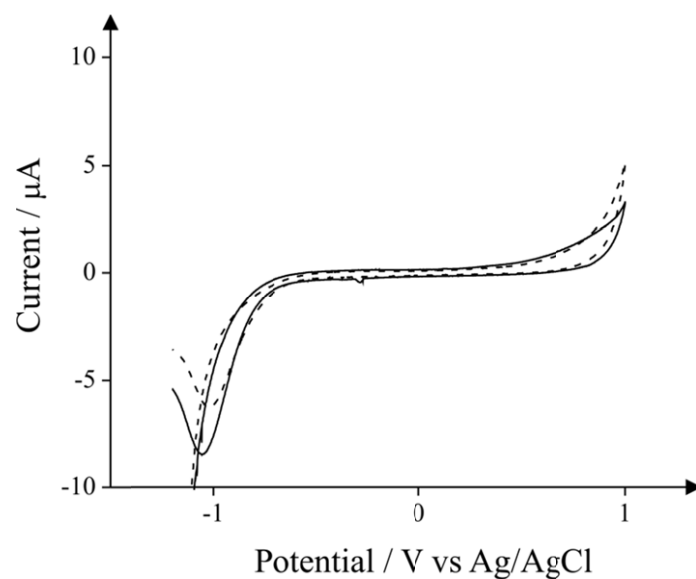


## Electronic Supporting Information (ESI)

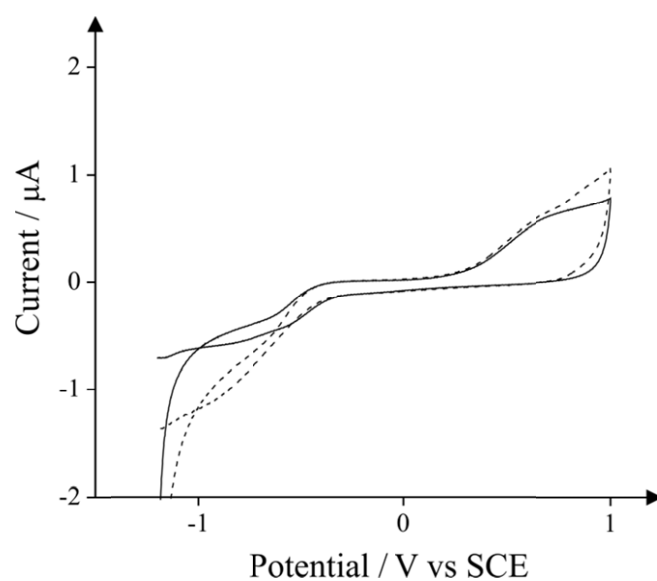
### Figure S1

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  morpholine in pH 10 carbonate buffer solution recorded using SPGE. Scan rate:  $50 \text{ mVs}^{-1}$  vs Ag/AgCl



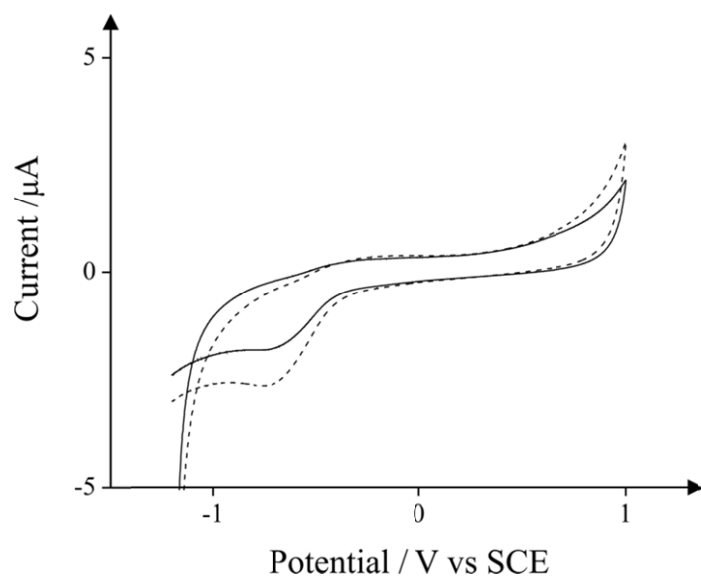
### Figure S2

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  morpholine in pH 10 carbonate buffer solution recorded using BDDE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



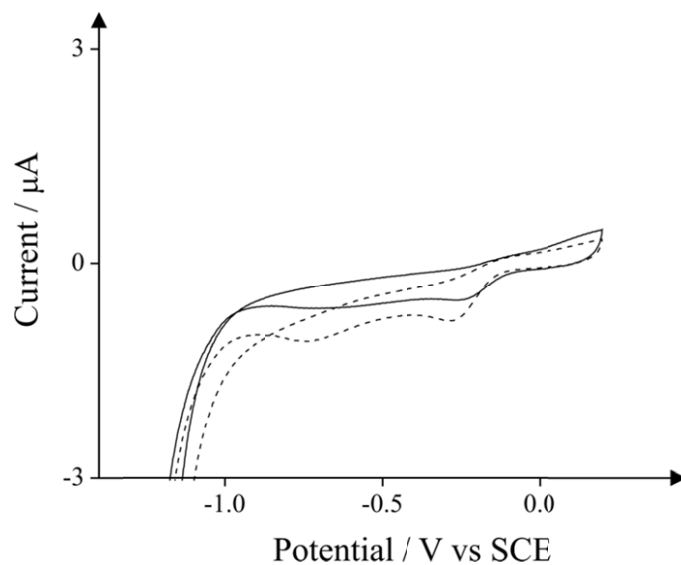
**Figure S3**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  morpholine in pH 10 carbonate buffer solution recorded using GCE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



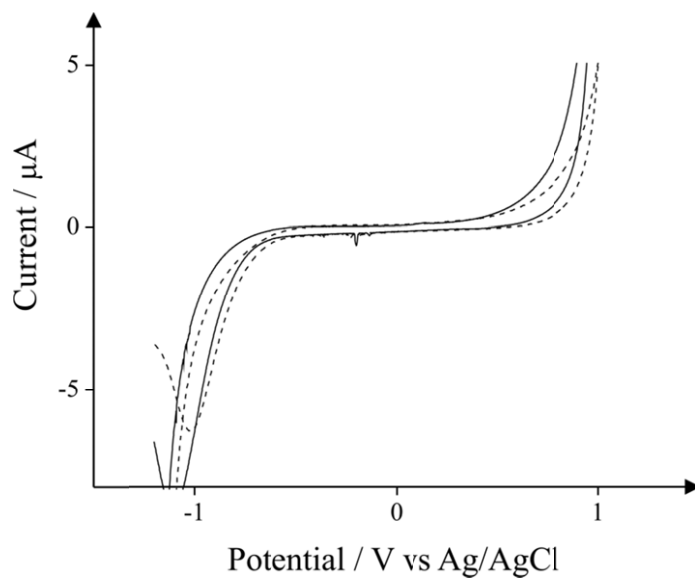
**Figure S4**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  morpholine in pH 10 carbonate buffer solution recorded using AuE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



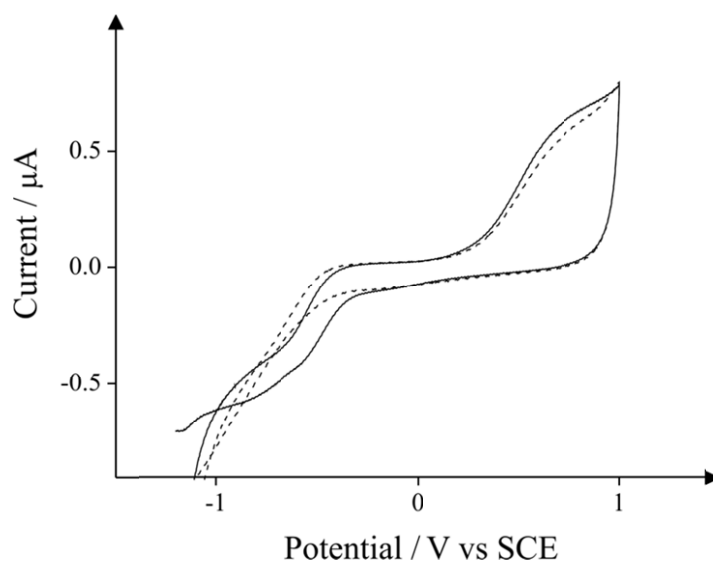
**Figure S5**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  cyclohexylamine in pH 10 carbonate buffer solution recorded using SPGE. Scan rate:  $50 \text{ mVs}^{-1}$  vs Ag/AgCl



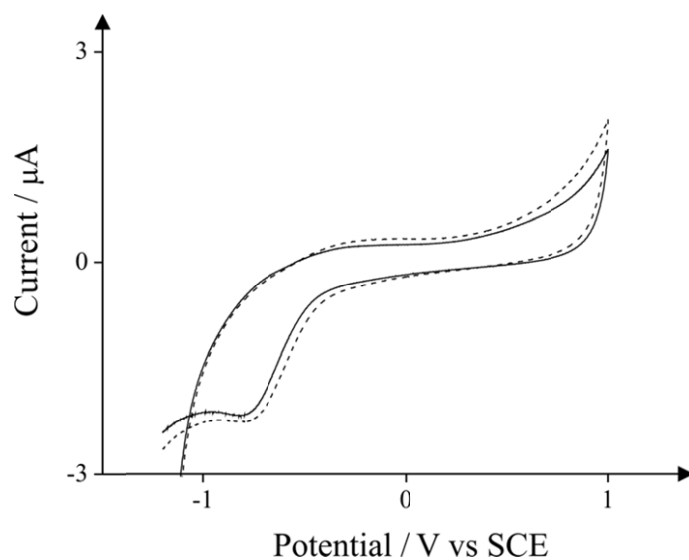
**Figure S6**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  cyclohexylamine in pH 10 carbonate buffer solution recorded using BDDE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



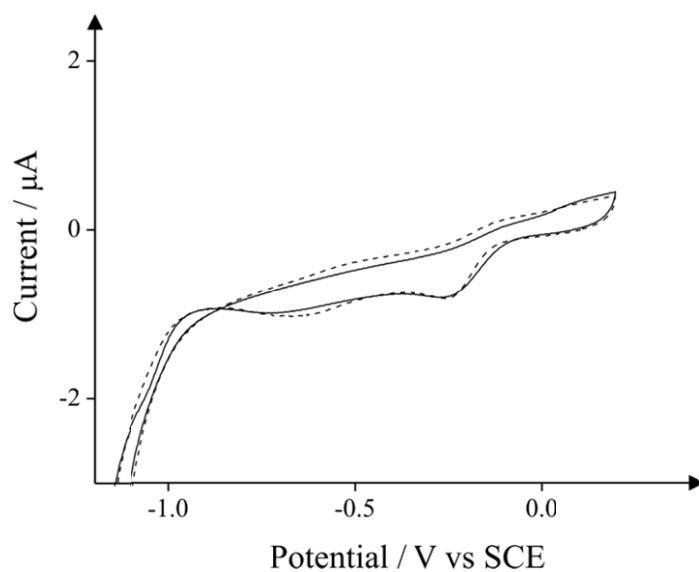
**Figure S7**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  cyclohexylamine in pH 10 carbonate buffer solution recorded using GCE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



**Figure S8**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of  $10 \text{ mgL}^{-1}$  cyclohexylamine in pH 10 carbonate buffer solution recorded using AuE. Scan rate:  $50 \text{ mVs}^{-1}$  vs SCE



### **pH study of the mediators**

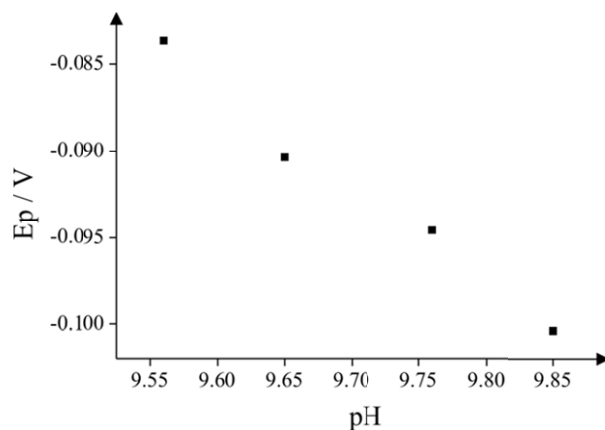
The plots of reduction peak potential  $E_p$  vs. pH for the mediators N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide and N,N'-(1,4-phenylene)dibenzenesulfonamide are shown in figure S9 and S10 respectively. In case of N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide (S9) the plot shows a linear range with a gradient of 0.055 ( $E/V = -0.055 + 0.444 E/pH$   $R^2=0.98$ ). In case of N,N'-(1,4-phenylene)dibenzenesulfonamide (S10) the plot shows a linear range with a gradient of 0.060 ( $E/V = -0.060 + 0.651 E/pH$   $R^2=0.99$ ). Such a value is close to that expected for 2 protons and 2 electrons process according to the electrochemical step (1) of the proposed mechanism (see Scheme 1) (59 mV per pH unit at 25 °C) as deduced from the following equation:

$$E = E^0 - 0.059 \frac{m}{n} pH \quad (11)$$

where  $E^0$  is the standard reduction potential,  $m$  and  $n$  are the number of protons and electrons participate in the reaction respectively and the other symbols have their usual meaning.

### Figure S9

Cyclic voltammetric responses obtained in carbonated buffer solution at different pH values. Plot of peak potential,  $E_p$ , as a function of pH for the electrochemical reduction of  $100 \mu\text{g mL}^{-1}$  N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide in carbonated buffer solution at different pH values. In all cases SPEs were utilised. Scan rate:  $50 \text{ mV s}^{-1}$  vs. Ag/AgCl



### Figure S10

Cyclic voltammetric responses obtained in carbonated buffer solution at different pH values. Plot of peak potential,  $E_p$ , as a function of pH for the electrochemical reduction of  $100 \mu\text{g mL}^{-1}$  N,N'-(1,4-phenylene)dibenzene-sulfonamide in carbonated buffer solution at different pH values. In all cases SPGEs were utilised. Scan rate:  $50 \text{ mV s}^{-1}$  vs. Ag/AgCl

