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Supporting Information

Efficiently catalytic Reduction of Azo Dyes by N,N-Dimethylformamide

Mediated by Viologen **

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Experimental Section

Materials and General Procedures:

8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid disodium salt (SNAZOXS²⁻), Congo Red (CR), Methyl Orange (MO), Nitrazin Yellow (NY), Beryllon II (Be) were selected as azo dye model compounds. The chemical structures of the dyes are illustrated in [Fig. S1](#). Dyes were purchased from Sigma and used without additional purification. Stock solutions of 2 mM were prepared in deionised water. The UV-Vis absorption spectra were recorded on a HITACHI U-3900 spectrophotometer and the fluorescence spectra were measured with a HITACHI F-4600 fluorescence spectrophotometer ($\lambda_{ex} = 330$ nm). The extent of fading of each dye was determined by the decrease in absorption at λ_{max} . Since dye solutions obey the Beer-Lambert law, the concentration of the residual dye could be determined spectrophotometrically. The decolorization of dye, expressed as dye decolorization (%), was calculated by means of the formula: decolorization (%) = $[(C_i - C_t)/C_i] \times 100$, where, C_i : initial concentration of the dye, C_t : dye

concentration along the time. The decolorization efficiency of each dye was shown as dye decolorization (%).

Analytical characterization was performed on a HPLC/MS (Agilent-1200 series) with a conventional C18 column, at room temperature and a mixed solvent of acetonitrile and water as eluent at the ratio of 20:80 (v/v) at 20 °C.

The reduction of azo dye by DMF: 1.3 mg dodV^{2+} was dissolved in 10 ml DMF- H_2O solvent with water contents of 80 % and stirred. Then, 0.5 ml prepared aqueous SNAZOXS $^{2-}$ solution (2 mM) was added dropwise at room temperature and heated at 104 °C for 15 min. The color of solution altered from red to colorless, indicating SNAZOXS have been reduced by using dioctadecylviologen as an electron transfer catalyst in the mixed solvent composed of N,N-dimethylformamide (DMF) and H_2O .

Anaerobic conditions were achieved by bubbling dry nitrogen through the solutions for 30 min before irradiation, and during each experiment a blanket of argon was maintained over the solution.

The reduction of azo dye by $\text{Na}_2\text{S}_2\text{O}_4$: 0.5 ml prepared aqueous SNAZOXS $^{2-}$ solution (2 mM) was added dropwise to the 5 ml aqueous solution containing $\text{Na}_2\text{S}_2\text{O}_4$ (0.2 mM or 2 mM) at room temperature, then the reaction mixture stirred for several minutes for further measurements. Upon reduction, the solution changed from red to yellow.

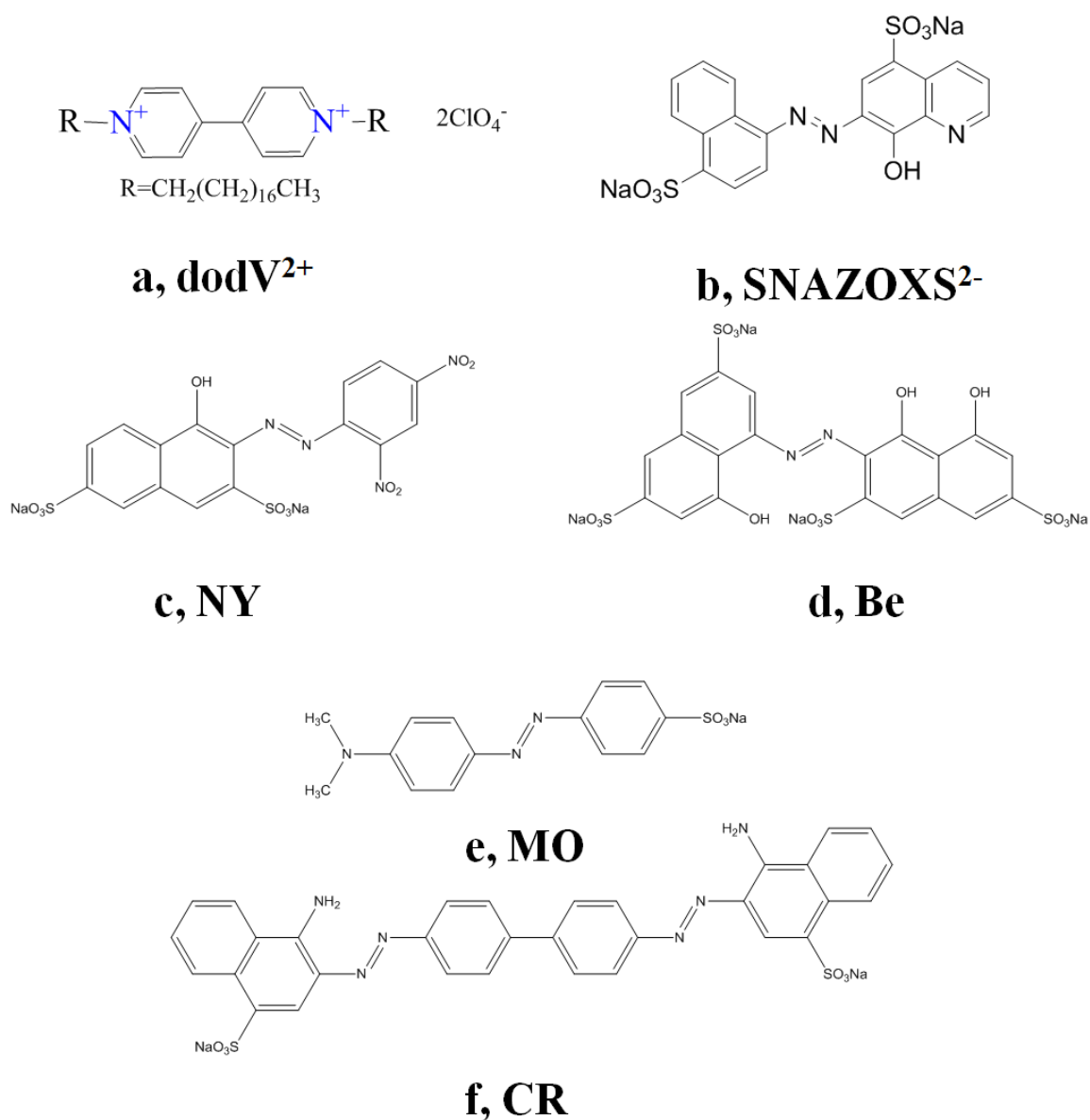


Figure S1. Structures of the catalyst and azo dyes used in this study: 1,1'-dioctadecyl-4,4'-bipyridinium diperchlorate(a, dodV²⁺); 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid disodium salt (b, SNAZOXS²⁻); nitrazin yellow (c, NY); beryllon II (d, Be); methyl orange (e, MO); congo red (f, CR).

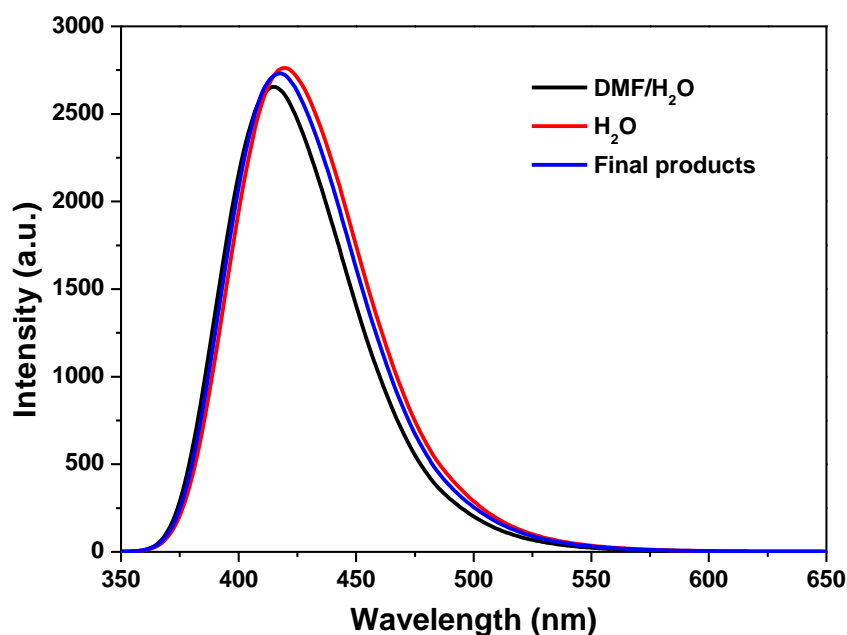


Figure S2. Fluorescence emission spectra of ANS in various solvents and final products of SNAZOXS²⁻ after refluxed with dodV²⁺ in DMF/H₂O.

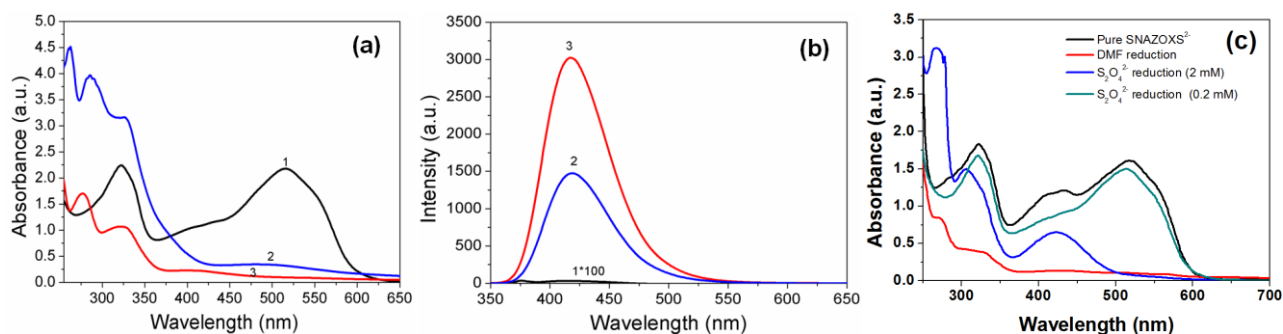


Figure S3. (a) UV-Vis absorbance spectra and (b) fluorescence emission spectra of 1. SNAZOXS²⁻; 2. SNAZOXS²⁻ after stirred at room temperature with Na₂S₂O₄ in DMF/H₂O mixtures; 3. SNAZOXS²⁻ after heated at 104 °C for 15 min with dodV²⁺ in DMF/H₂O mixtures. (c) UV-Vis absorbance spectra of SNAZOXS²⁻ before and after reduced by DMF or Na₂S₂O₄.

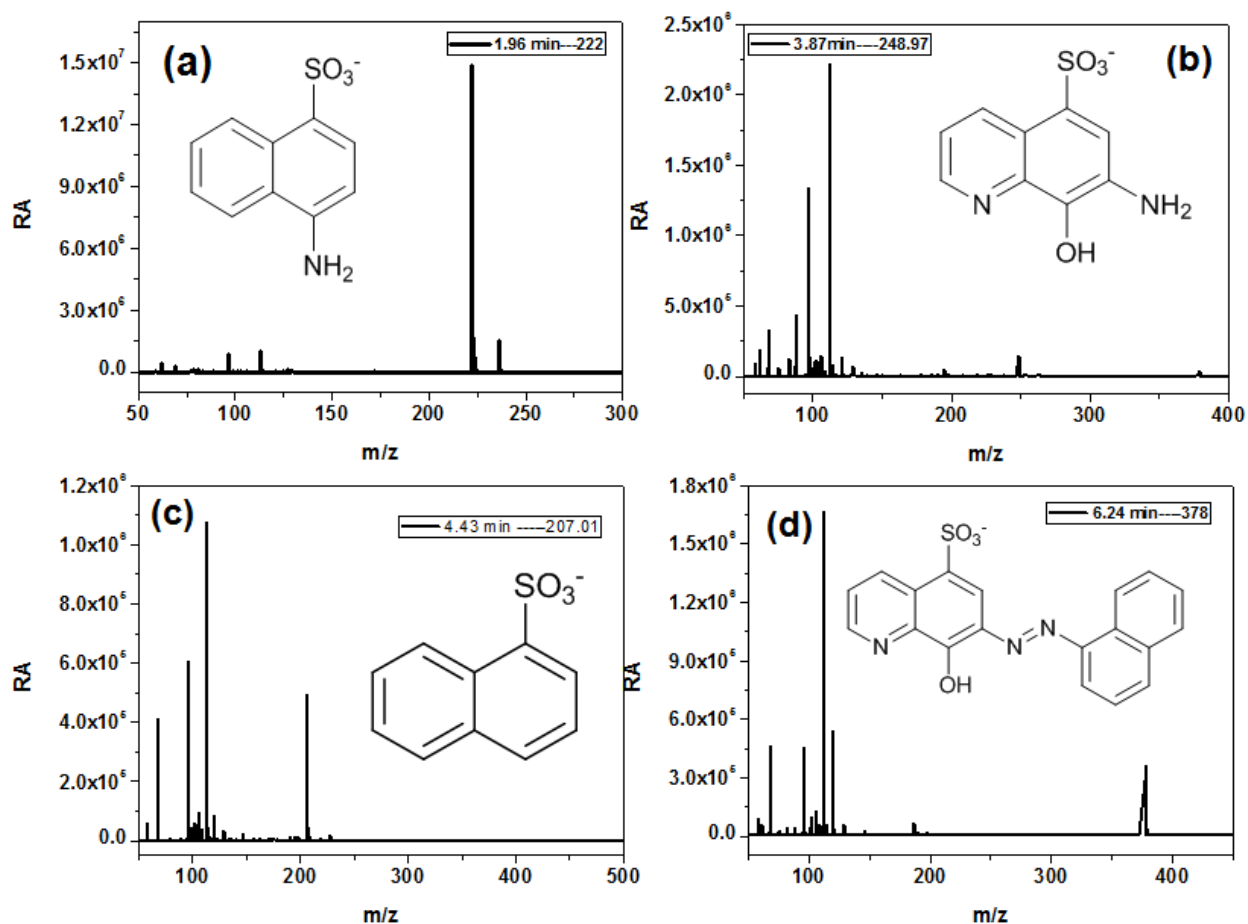


Figure S4. Mass spectra of the SNAZOXS²⁻ after heated at 104 °C for 15 min with dodV²⁺ eluting at different time (c-f): 1.95, 3.87, 4.43 and 6.24 min. ([SNAZOXS²⁻] = 0.2 mM).

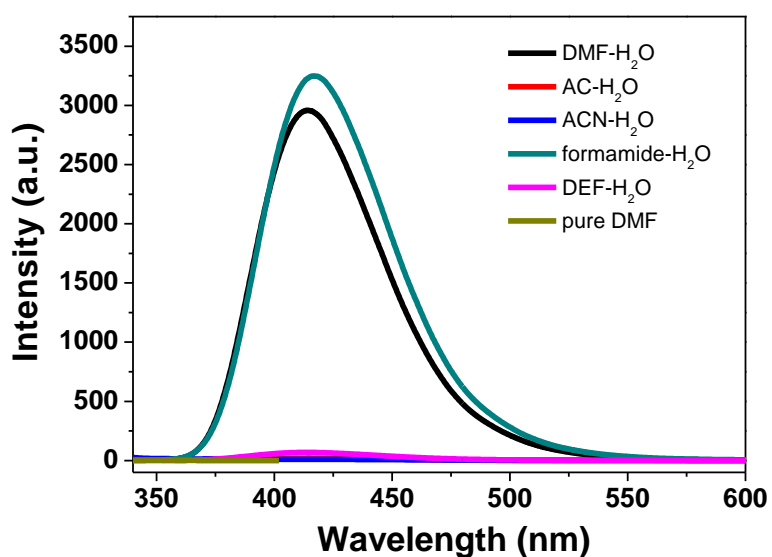


Figure S5. Fluorescence emission spectra of SNAZOXS²⁻ after heated at 104 °C for 15 min with dodV²⁺ in different solvent systems.

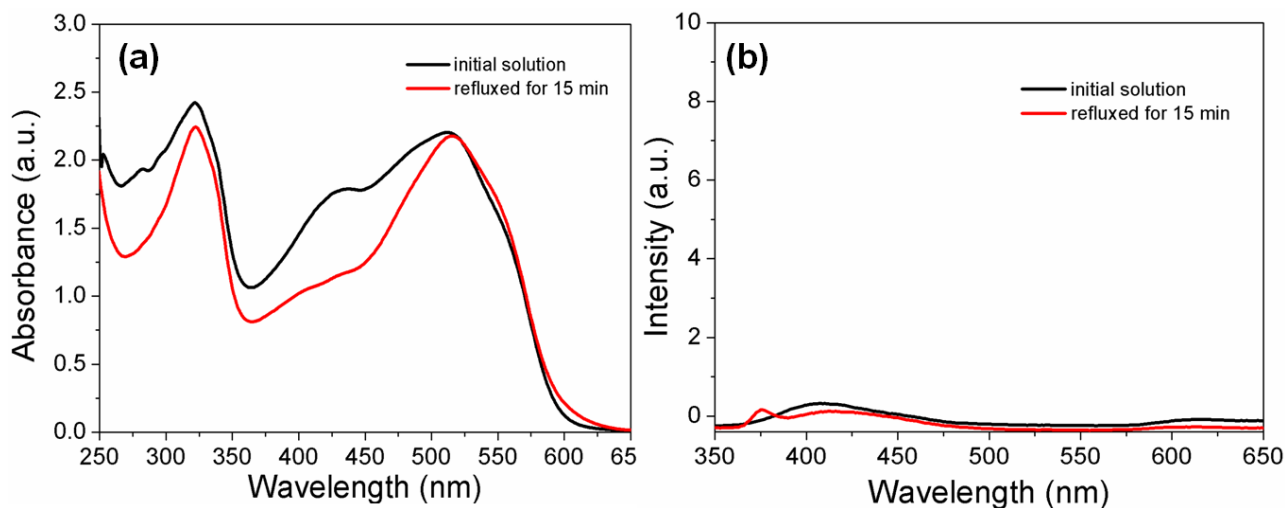


Figure S6. (a) UV-Vis absorbance spectra and (b) fluorescence emission spectra of SNAZOXS²⁻ before and after heated at 104 °C for 15 min without dodV²⁺.

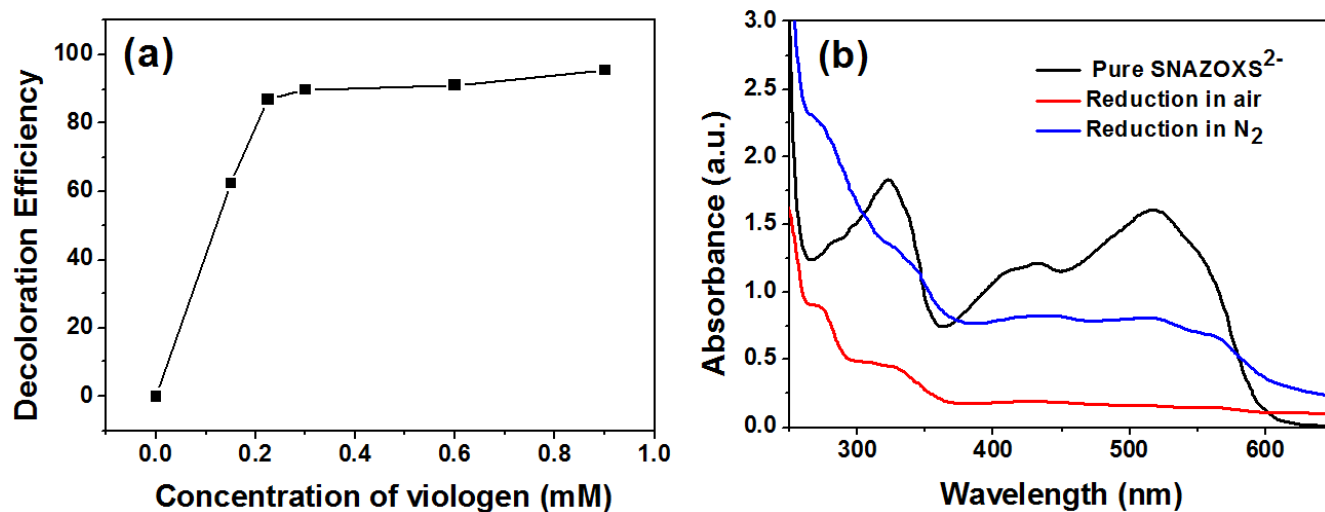


Figure S7. (a) The effect of viologen concentration on the decoloration efficiency of SNAZOXS²⁻. ($C_{\text{SNAZOXS}2^-} = 2 \text{ mM}$). (b) UV-Vis absorbance spectra of SNAZOXS²⁻ before and after heated at 104 °C for 15 min with dodV²⁺ in DMF/H₂O mixtures with or without O₂.

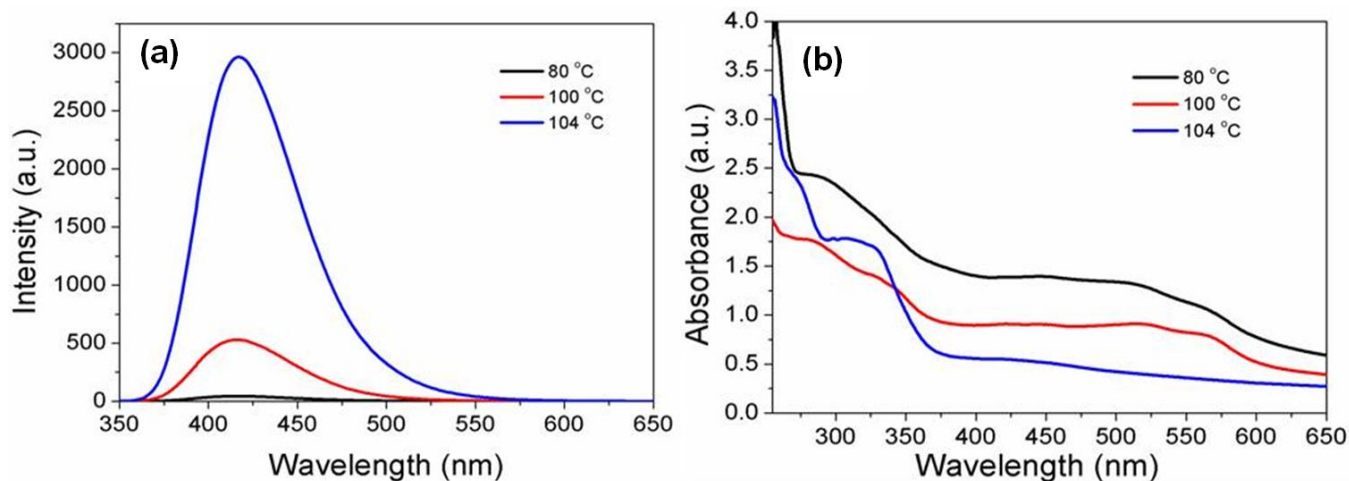


Figure S8. (a) Fluorescence emission spectra and (b) UV-Vis absorbance spectra of SNAZOXS²⁻ after heated at 104 °C for 15 min with dodV²⁺ at different temperature.

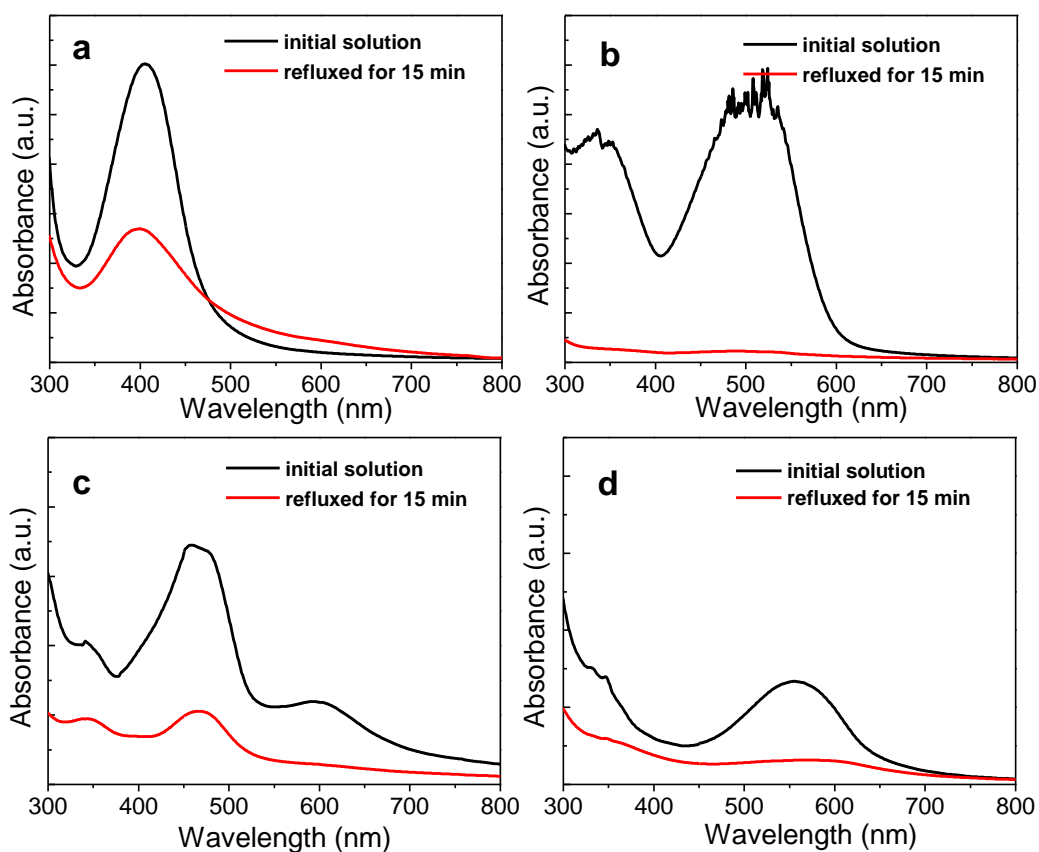


Figure S9. UV-Vis absorbance spectra of MO (a), CR (b), NY (c) and Be (d) before and after heated at 104 °C for 15 min with dodV²⁺ in DMF/H₂O mixture.