Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Continuous synthesis of hexanitrostilbene by difunctional electrochemical reactor

Supporting Information

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1.1 Electrochemical conversion of TNT

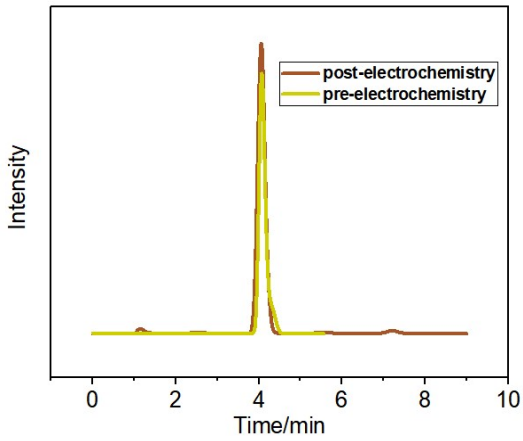

Fig. S1 Liquid phase diagram of TNT pre-electrochemistry and post-electrochemistry.

1.2 Electrochemical conversion of TNBCl

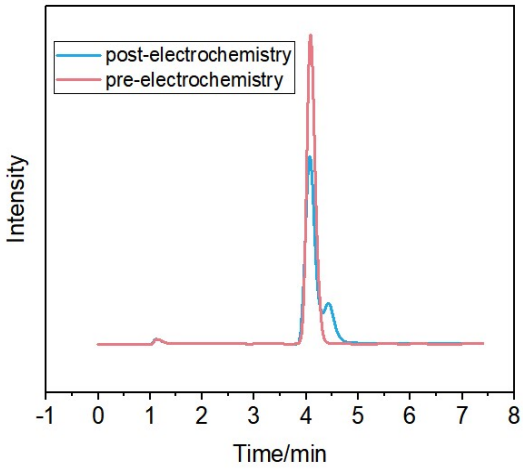

Fig. S2 Liquid phase diagram of TNBCl pre-electrochemistry and post-electrochemistry.

1.3 Hydrogen nuclear magnetic spectra of TNT

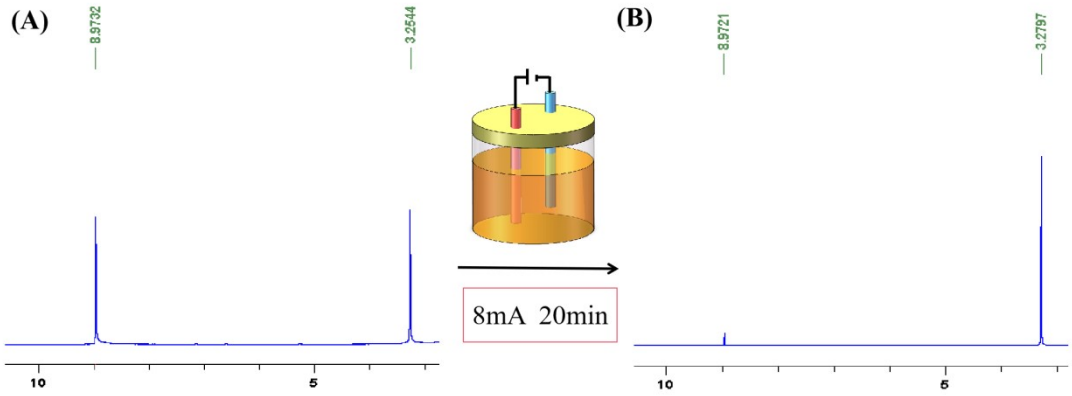

Fig. S3 (A) Hydrogen nuclear magnetic spectra of TNT pre-electrochemistry (500 MHz, DMSO-d6) δ = 8.9732, 3.2544. (B) Hydrogen nuclear magnetic spectra of TNT post-electrochemistry (500 MHz, DMSO-d6) δ = 8.9721, 3.2797.

1.4 Hydrogen nuclear magnetic spectra of TNBCl

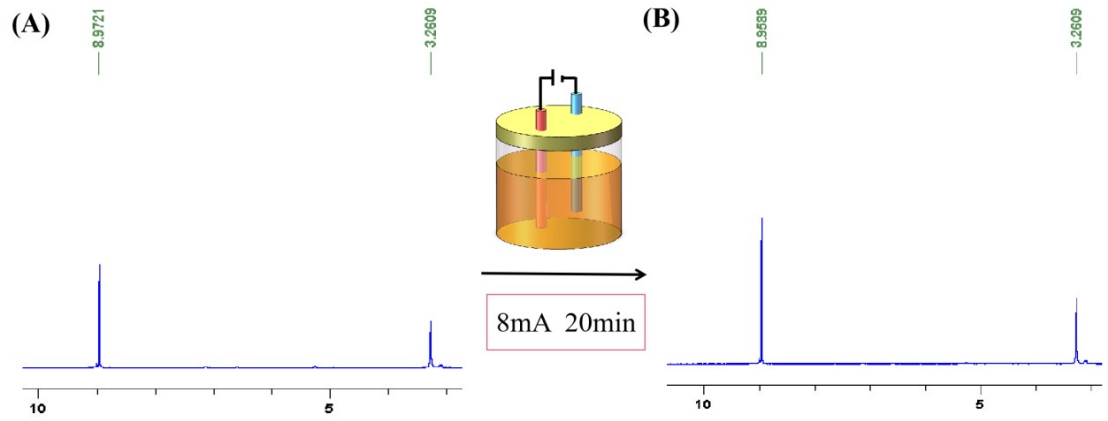

Fig. S4 (A) Hydrogen nuclear magnetic spectra of TNBCl pre-electrochemistry (500 MHz, DMSO-d6) δ = 8.9721, 3.2609. (B) Hydrogen nuclear magnetic spectra of TNBCl post-electrochemistry (500 MHz, DMSO-d6) δ = 8.9589, 3.2609.

1.5 Hydrogen nuclear magnetic spectra of HNBB

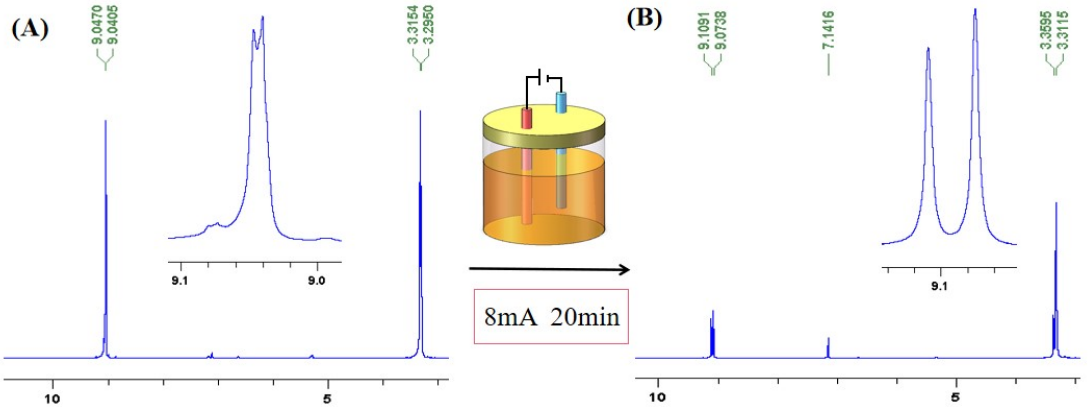

Fig. S5 (A) Hydrogen nuclear magnetic spectra of HNBB pre-electrochemistry (500 MHz, DMSO-d6) δ = 9.0470, 3.3154. (B) Hydrogen nuclear magnetic spectra of HNBB post-electrochemistry (500 MHz, DMSO-d6) δ = 9.1091, 9.0738, 7.1416, 3.3595. The NMR peak of HNS (δ = 9.1091, 7.1416) appeared in the electrochemical products of HNBB, but not in the electrochemical products of TNT and TNBCl.

1.6 Details about Faradaic efficiency calculations.

$$\text{FE (\%) for HNS production} = \frac{mol\ of\ HNS\ formed \times 96485}{Q/2} \times 100\%$$

At a constant current of 8 mA for 900 s, Q =7.2 C. Due to a conversion rate of 74.33%, 4.4 mM HNBB is converted to 0.0327 mmol of HNS in 10 ml of DMSO.

$$\text{FE} = \frac{0.0327 \times 0.001 \times 96485 \times 2}{7.2} = 87.65\%$$

1.7 Standard curve of HNS and HNBB

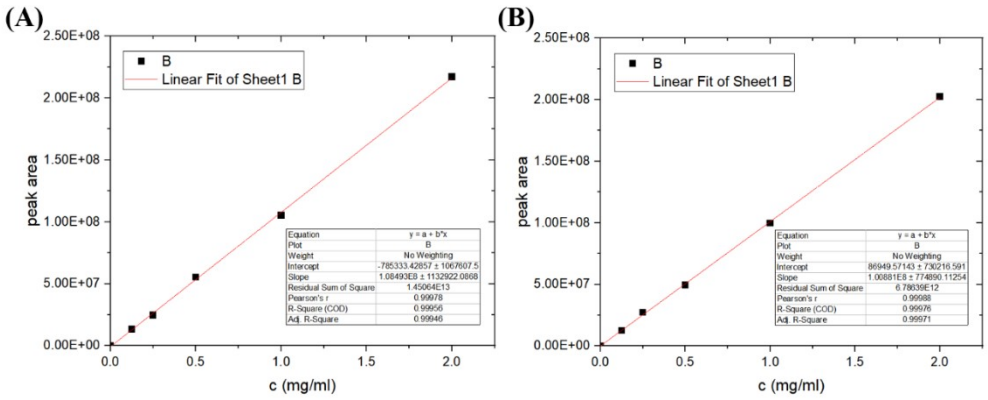

Fig. S6 (A) The standard curve of HNS, y=1.085 × 10^8 x-785333 (R^2 = 0.999). (B) The standard curve of HNBB, y=1.009 × 10^8 x-86949(R^2 = 0.999).

2.1 Mixing effect of static mixer

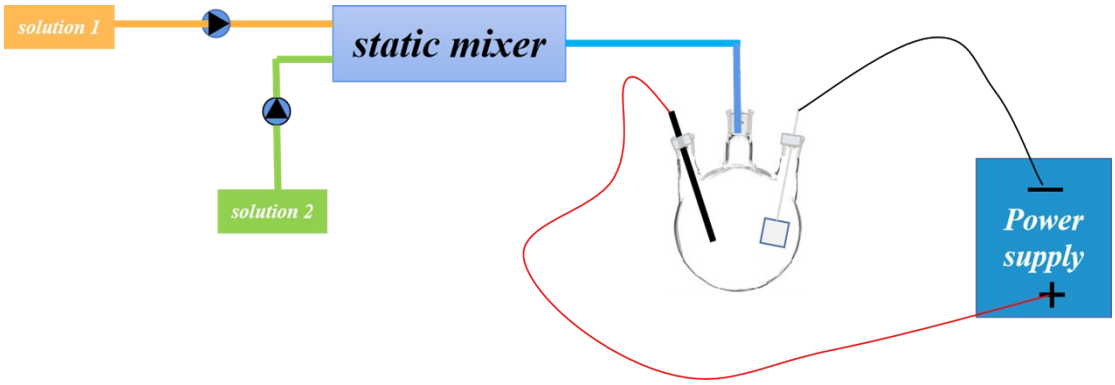

Fig. S7 Segmented preparation diagram.

2 g TNT was dissolved in 11 mL MeOH and 22 mL THF as solution 1, fed at the rate of 1.5 mL/s. 11 mL 5% NaClO solution was added to 10 mL water as solution 2, fed at the rate of 1 mL/s. 0.15 g $^nBu_4NBF_4$ and 0.05 g DABCO were added in three-neck flask, filtration after 1.5 h under 8 mA current.

3 Laboratory preparation

Fig. S8 Physical diagram of the electrochemical reactor.

4 NMR spectra

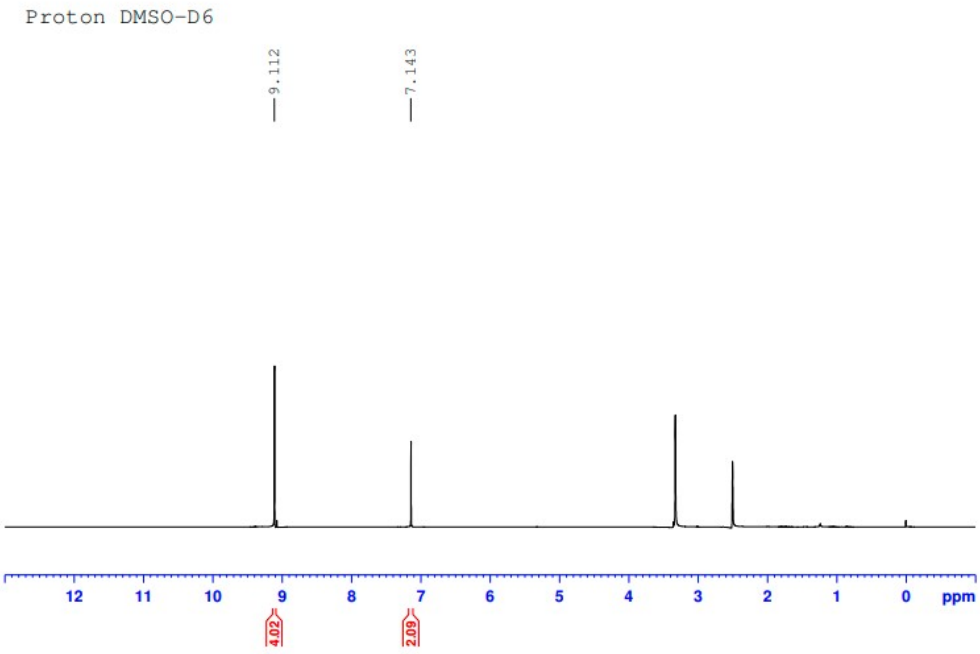

Fig. S9 Hydrogen nuclear magnetic spectra of HNS synthesized by electrochemical reactor
1H NMR (500 MHz, DMSO-d6) δ = 7.143 (s, 2H), 9.112 (s, 4H).

5 Optimization of feed flow rate

Table S2 The influence of flow rate on yield of HNS synthesized by TNT in one step

Entry	Flow rate of TNT (mL/s)	Flow rate of NaClO (mL/s)	Reaction time/h	$^{n}Bu_4NBF_4$/g	DABCO/g	Current/A	Yield/%
1	1	0.7	0.5	0.04	0.02	0.008	51.21±0.39
2	1.5	1	0.5	0.04	0.02	0.008	58.53±0.26
3	2	1.4	0.5	0.04	0.02	0.008	53.78±0.18
4	2.5	1.75	0.5	0.04	0.02	0.008	49.91±0.27

Notes: According to the conversion relationship between flow rate and flow velocity，$Q = v \times S$. Flow rate: 1 mL/s, Pipe diameter: 1.6 mm. 1 $cm^3/s = v*\pi*0.08*0.08$, about 0.5 m/s. The velocities for solution 1 are simulated at 0.5 m/s, 0.75 m/s, 1.0 m/s, and 1.25 m/s in CFD. Similarly, the velocities for solution 2 are simulated at 0.35 m/s, 0.5 m/s, 0.75 m/s, and 0.87 m/s.

The flow rate ratio was kept consistent with the volume ratio. 2 g TNT was dissolved in 11 mL MeOH and 22 mL THF as solution 1, 11 mL 5% NaClO solution was added to 10 mL water as solution 2, 0.04 g $^{n}Bu_4NBF_4$ and 0.02 g DABCO were added. The reaction continued for 30 min and the constant current was 8 mA, the pH of solution was controlled to be 10 - 10.5. To prevent HNS from blocking the microchannels, the prepared solution was subjected to ice water bath.