

## Electronic Supporting Information (ESI)

### An environment friendly electrochemical synthesis of 1,1,4,4-tetramethyl-2-tetrazene energetic materials from undimethylhydrazine

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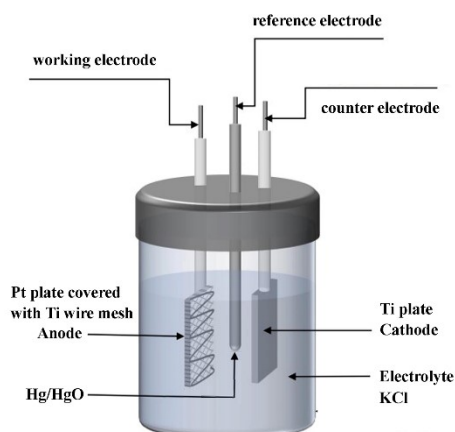


Fig. S1 The diagram of a representative three-electrodes electrochemical synthesis system.

GC-MS data were recorded on Shimadzu QC-MS 2010PLUS\*. The temperature of the column box was set at 40 °C, and the temperature of the injection port was 180 °C. The temperature program is 10°C/min heating rate from 40°C to 150°C and 15°C/min

heating rate from 150°C to 200°C.

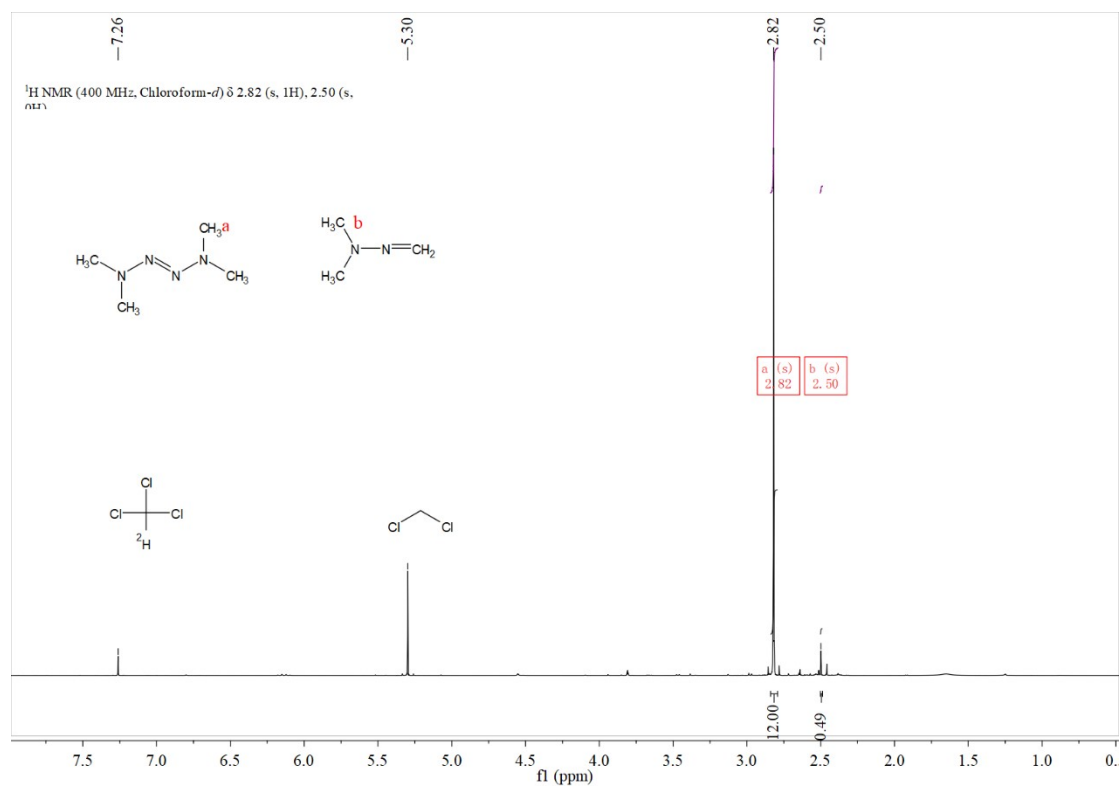
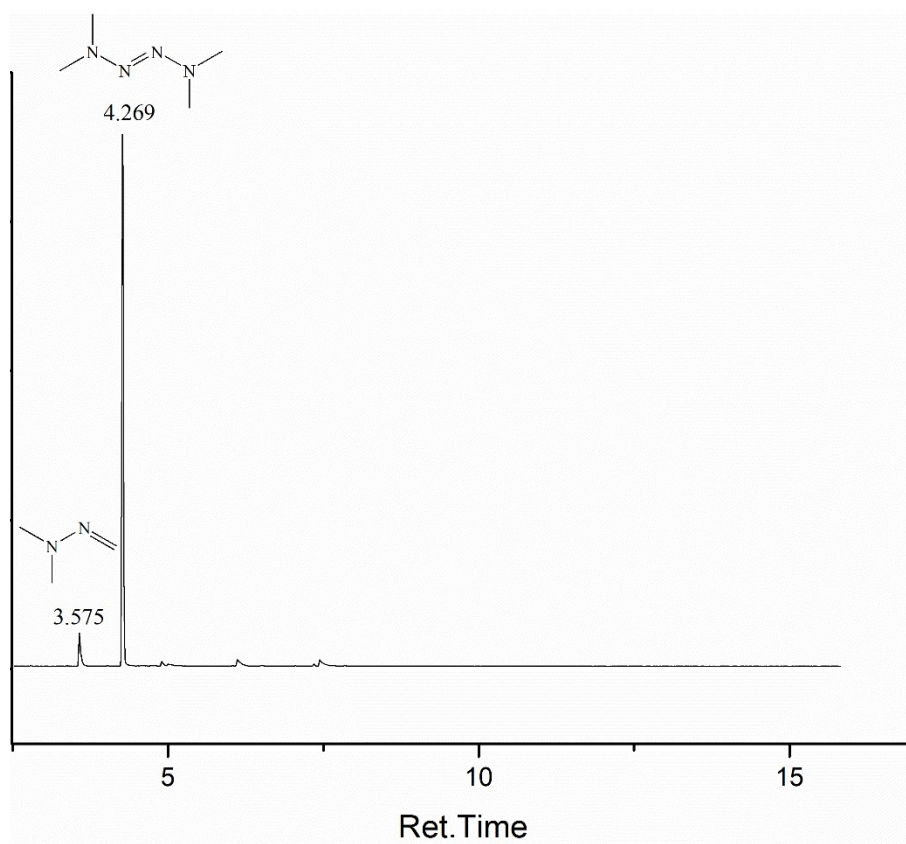


Fig. S2 GC-MS (top) and  $^1\text{H NMR}$  (bottom) of products in  $\text{CDCl}_3$  at 293 K with the electrodes of

Pt anode and C cathode)

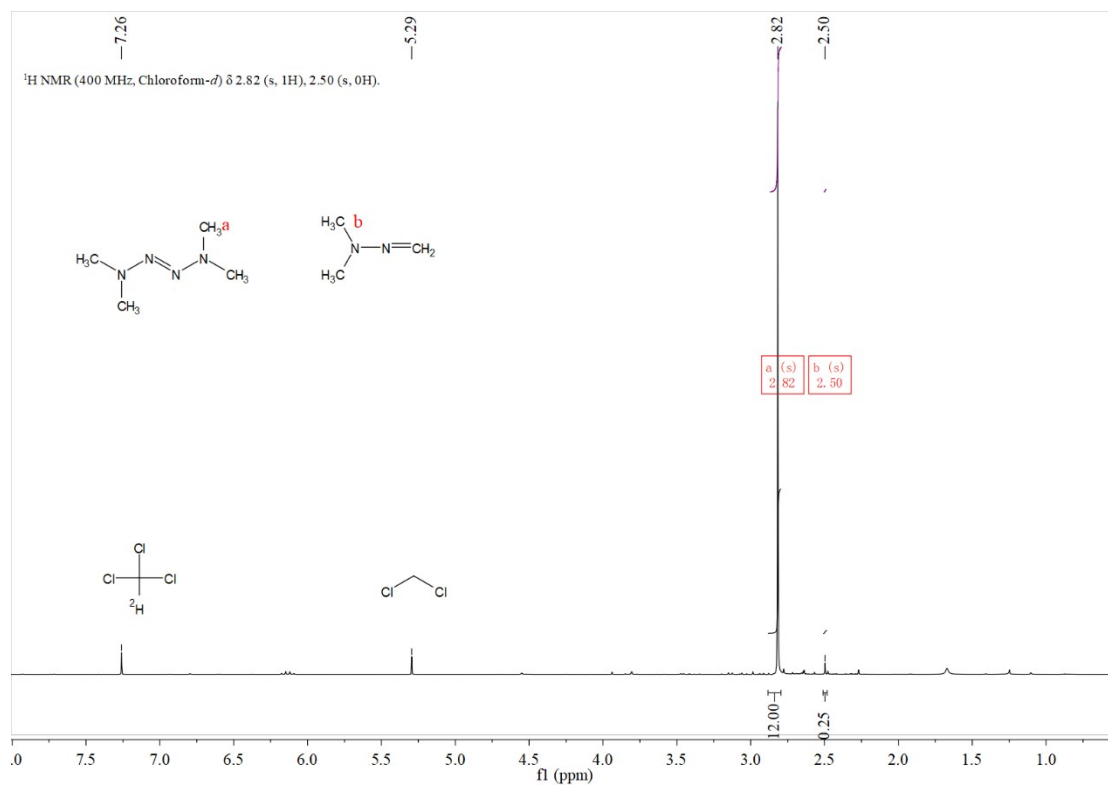
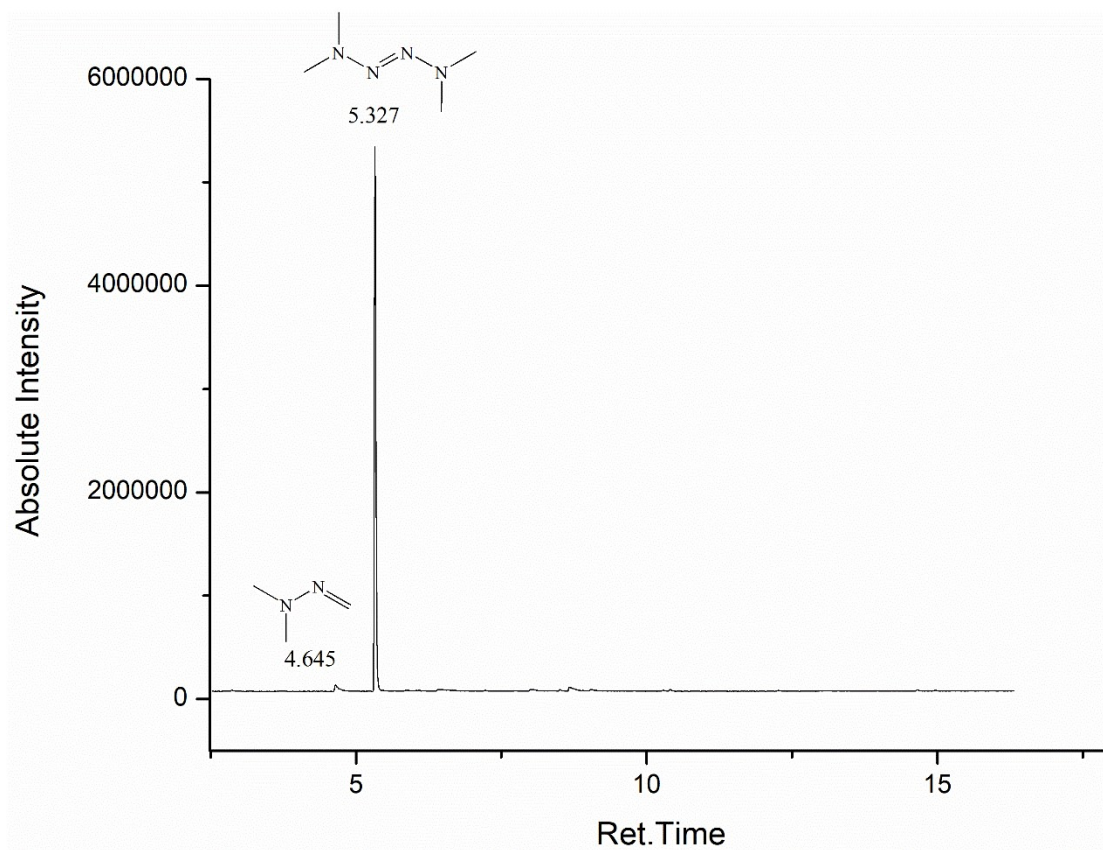


Fig. S3 GC-MS (top) and  $^1\text{H}$  NMR (bottom) of products in  $\text{CDCl}_3$  at 293 K with the electrodes of Pt anode and Ti cathode)

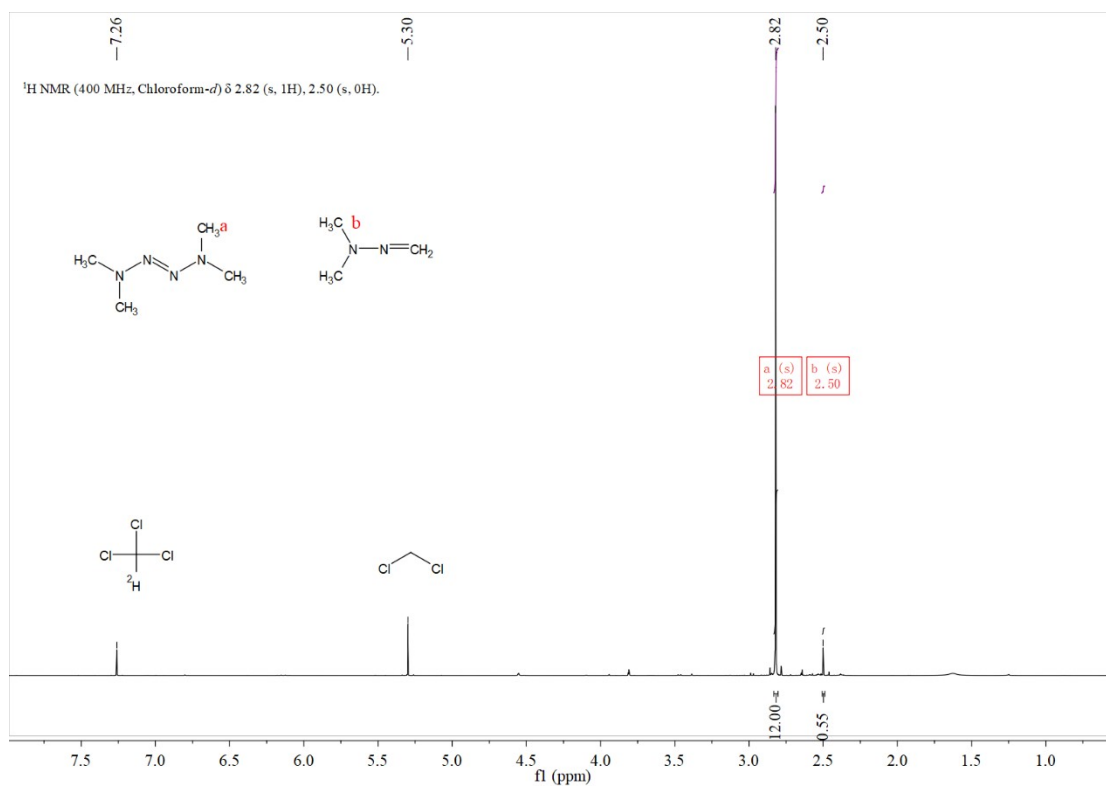
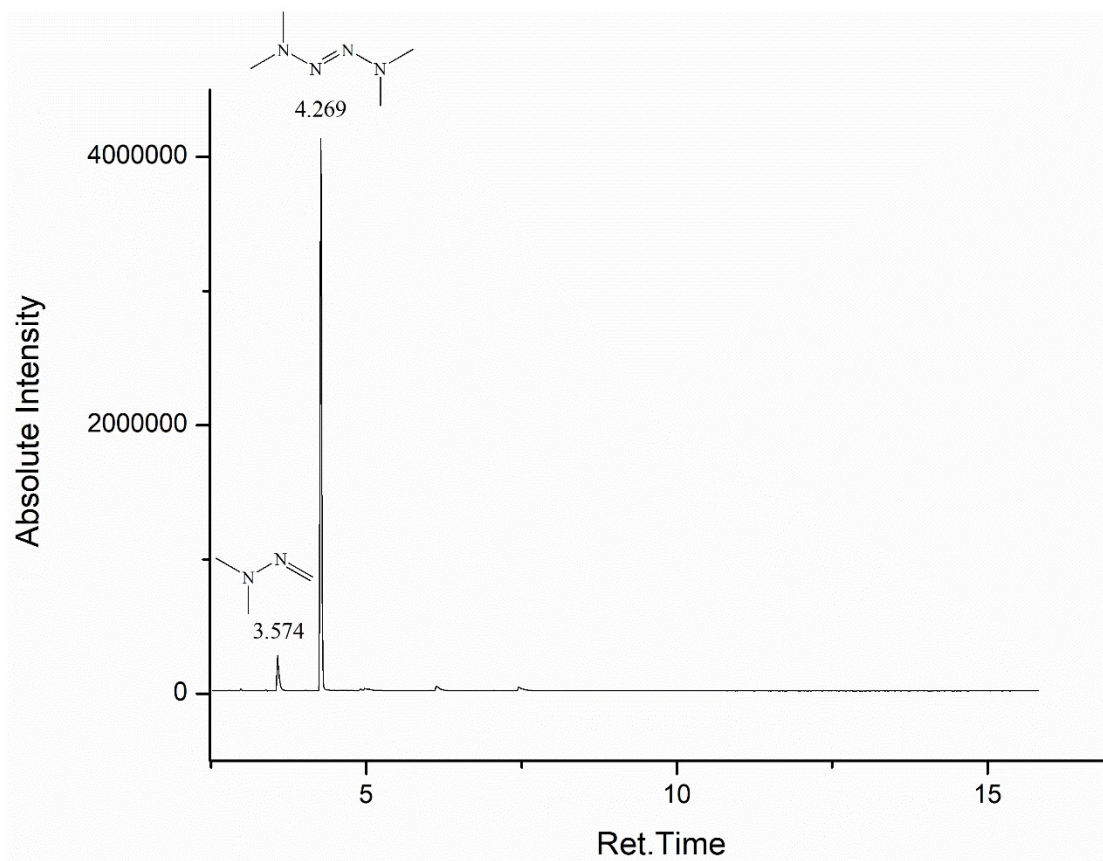


Fig. S4 GC-MS (top) and  $^1\text{H NMR}$  (bottom) of products in  $\text{CDCl}_3$  at 293 K with the electrodes of Au anode and C cathode

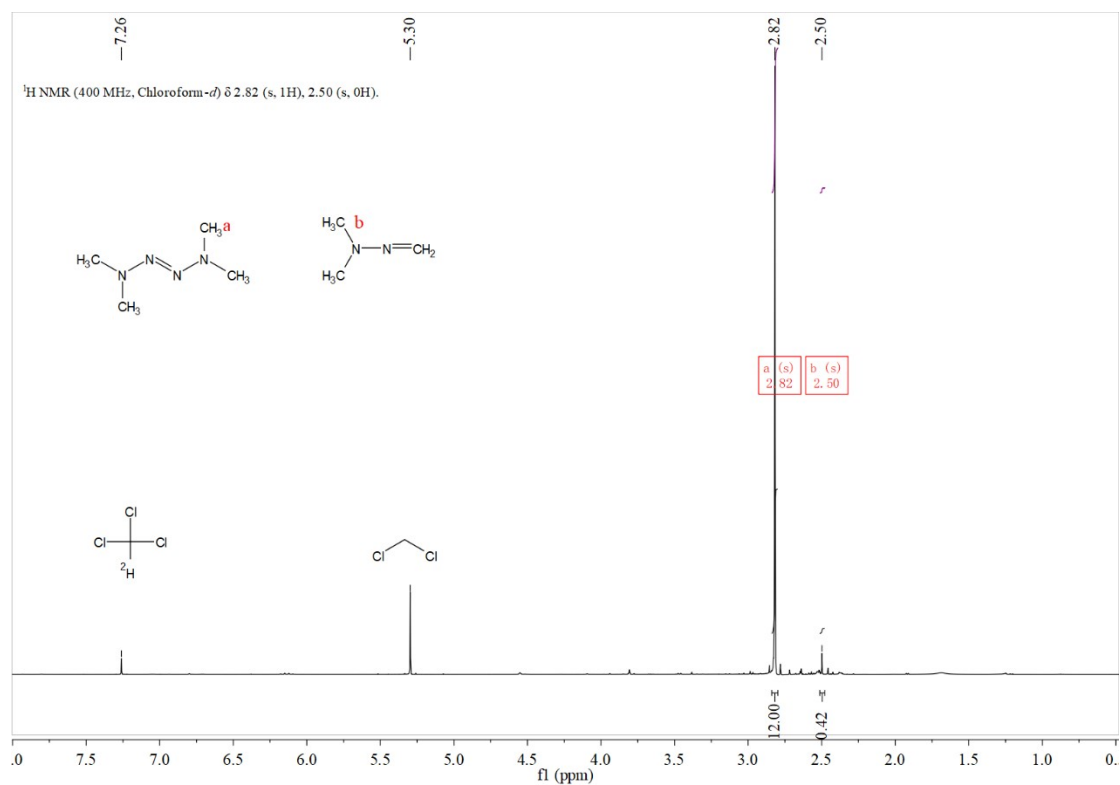
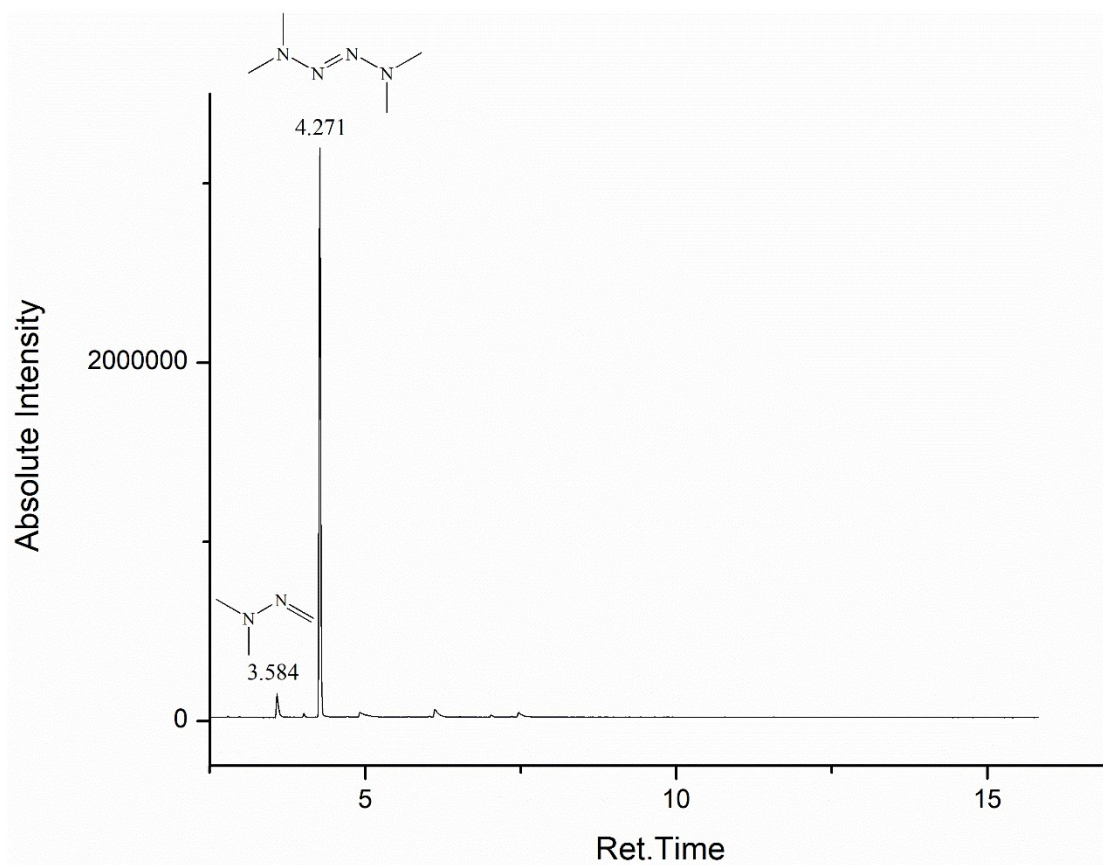


Fig. S5 GC-MS (top) and  $^1\text{H}$  NMR (bottom) of products in  $\text{CDCl}_3$  at 293 K with the electrodes of RuIr@Ti anode and C cathode



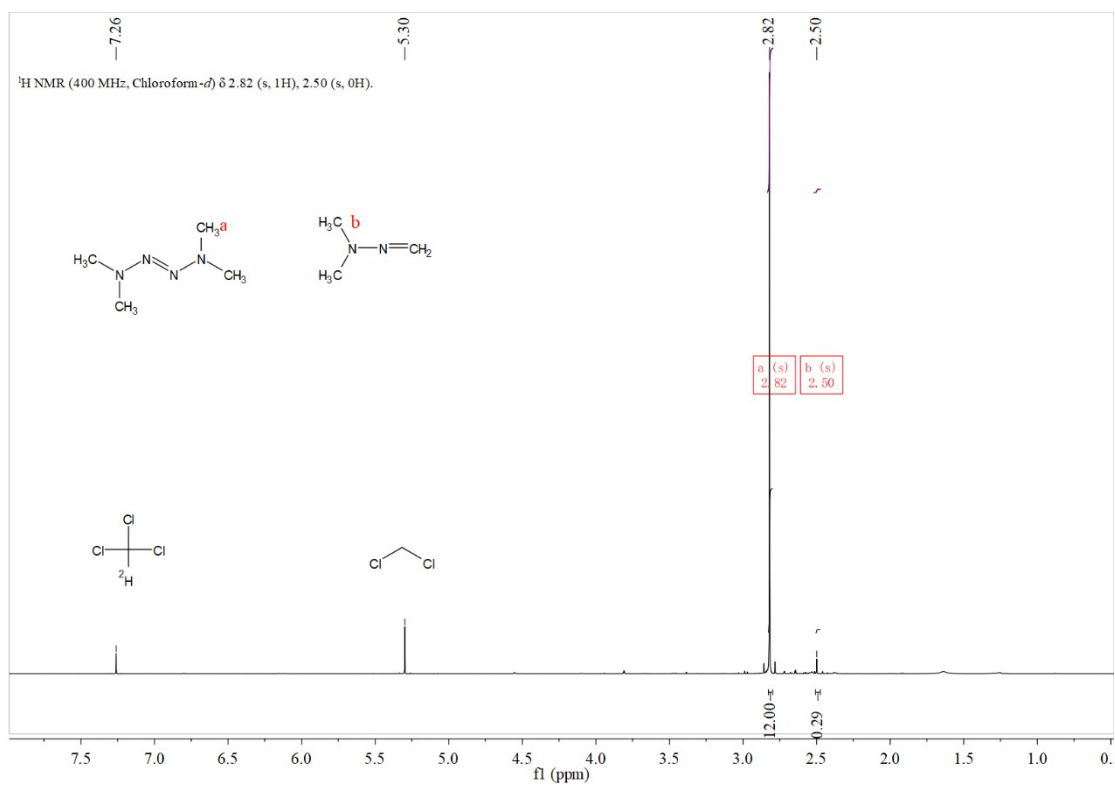
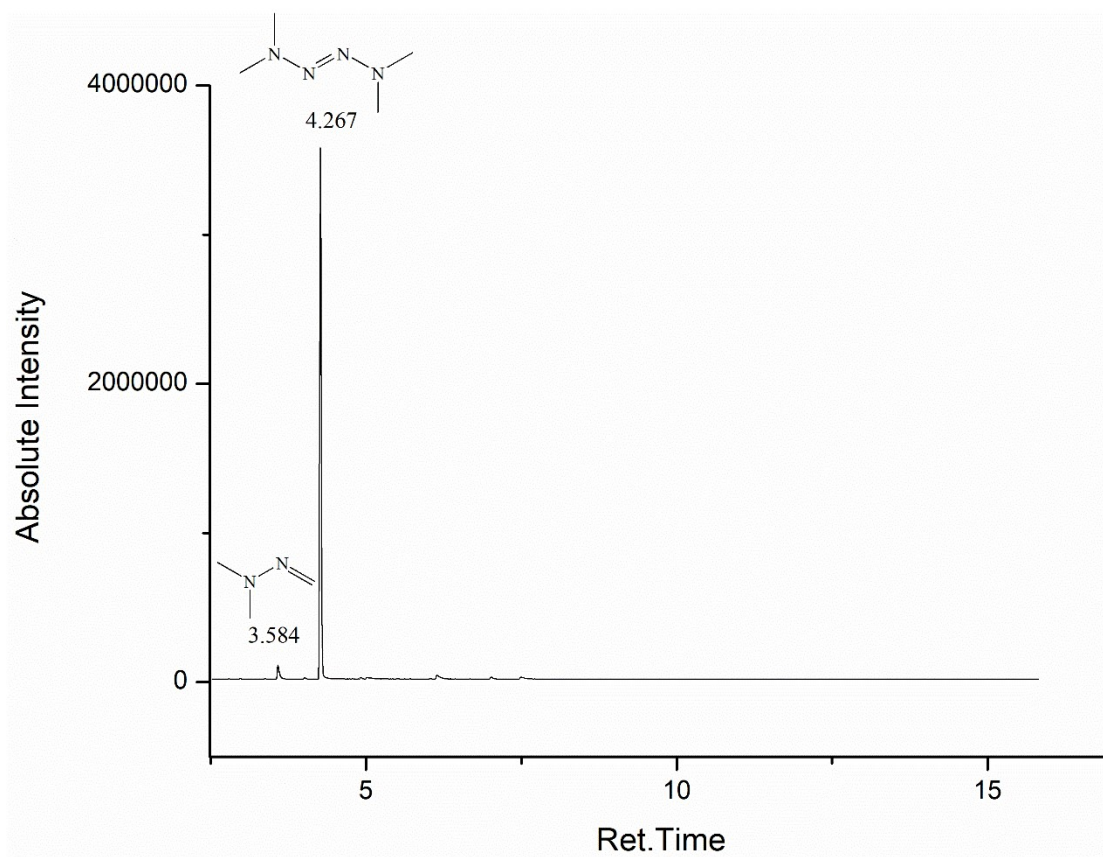


Fig. S6 GC-MS (top) and  $^1\text{H}$  NMR (bottom) of products in  $\text{CDCl}_3$  at 293 K with the electrodes of RuIr@Ti anode and Ti cathode

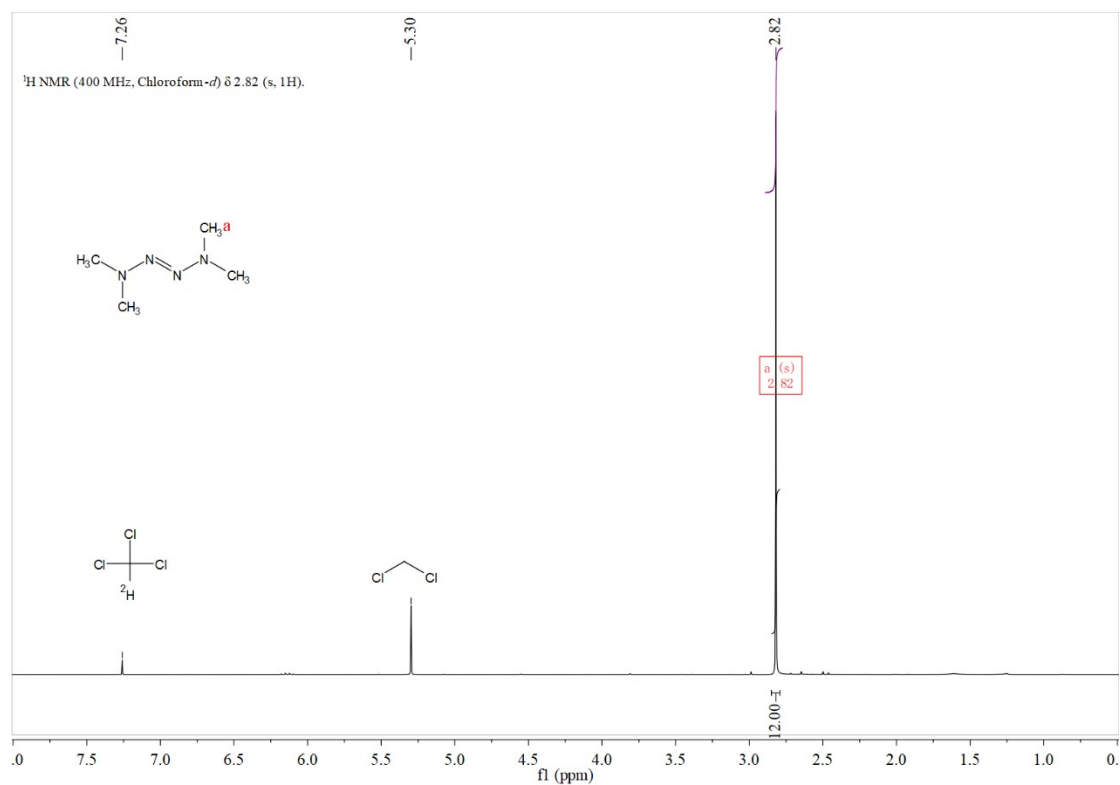
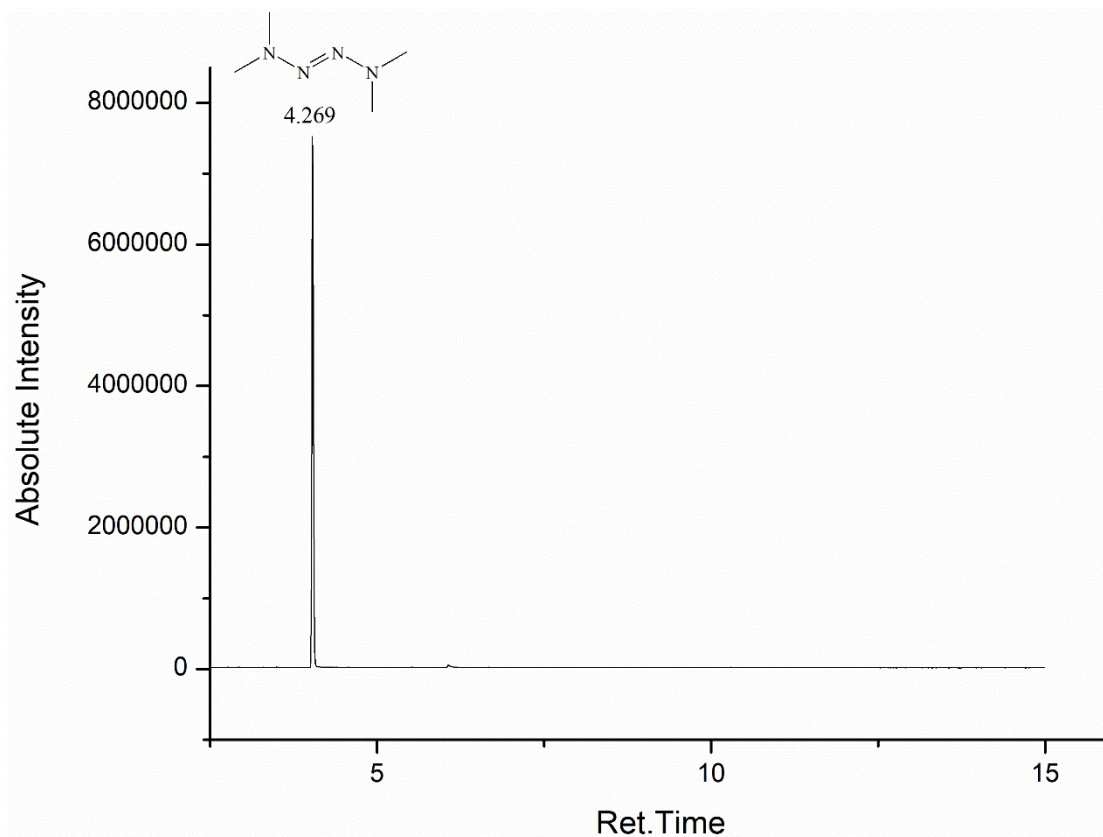


Fig. S7 GC-MS (top) and <sup>1</sup>H NMR (bottom) of products in CDCl<sub>3</sub> at 293 K with the electrodes of Ti-WM/Pt anode and Ti cathode.

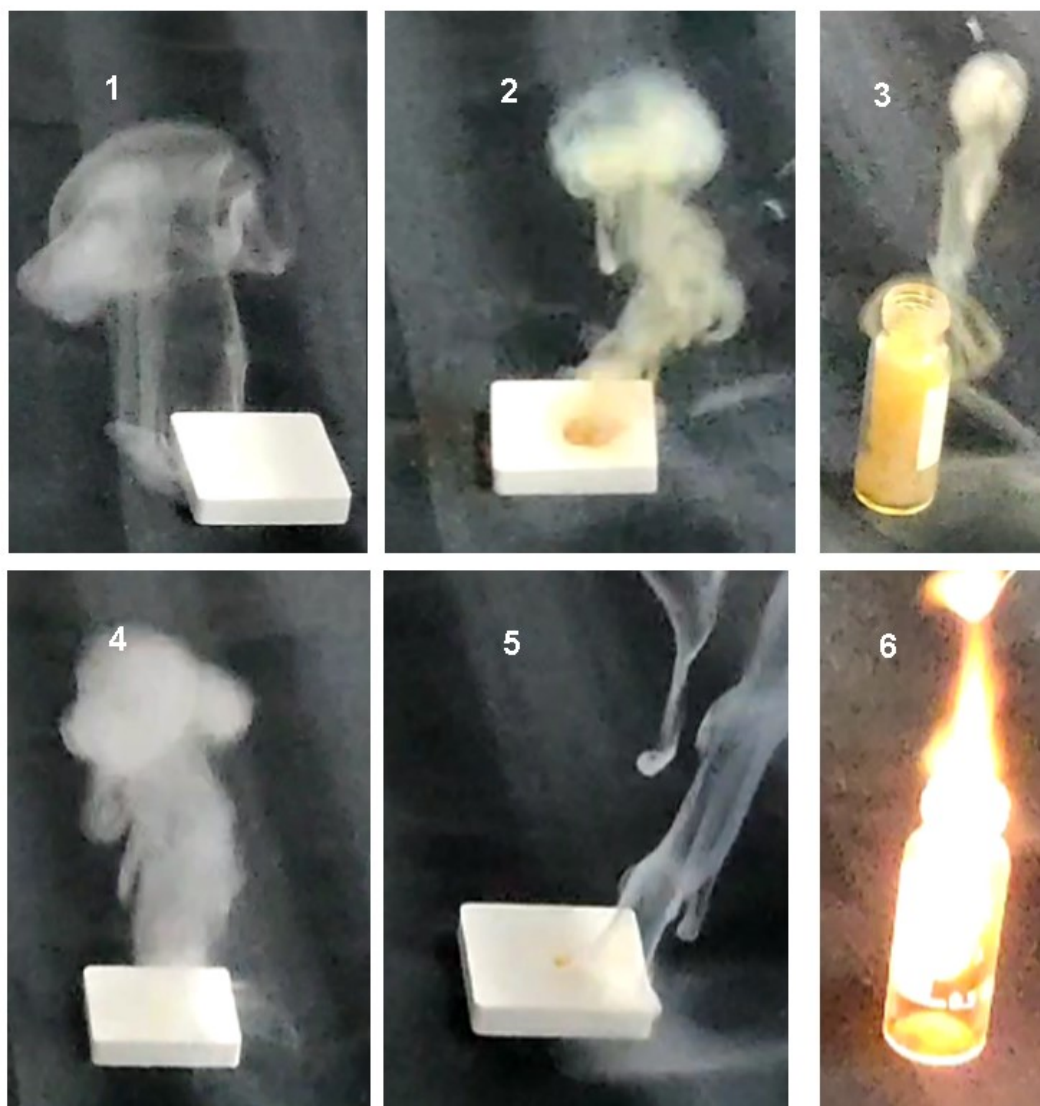


Fig. S8 Hypergolicity test of TMTZ and UDMH with oxidizers  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$  and  $\text{N}_2\text{O}_4$ : (1) TMTZ/ $\text{H}_2\text{O}_2$ , (2) TMTZ/ $\text{HNO}_3$ , (3) TMTZ/ $\text{N}_2\text{O}_4$ , (4) UDMH/ $\text{H}_2\text{O}_2$ , (5) UDMH/ $\text{HNO}_3$ , (6) UDMH/ $\text{N}_2\text{O}_4$ .

**Table S1.** Hypergolicity data of TMTZ and UDMH with oxidizers  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$  and  $\text{N}_2\text{O}_4$ .

Mixtures	Contact time (s)	Ignition time (s)	Ignition delay time (s)
TMTZ/ $\text{H}_2\text{O}_2$	4.976	5.457	0.481
TMTZ/ $\text{HNO}_3$	9.616	9.757	0.140
TMTZ/ $\text{N}_2\text{O}_4$	3.091	3.151	0.060
UDMH/ $\text{H}_2\text{O}_2$	22.744	22.962	0.218
UDMH/ $\text{HNO}_3$	8.122	8.182	0.060
UDMH/ $\text{N}_2\text{O}_4$	5.257	5.315	0.058

[1]. Hampton C, Ramesh K, Smith J, Importance of chemical delay time in understanding hypergolic ignition behaviors. 41st Aerospace Sciences Meeting and Exhibit, AIAA2003-1359, 2003



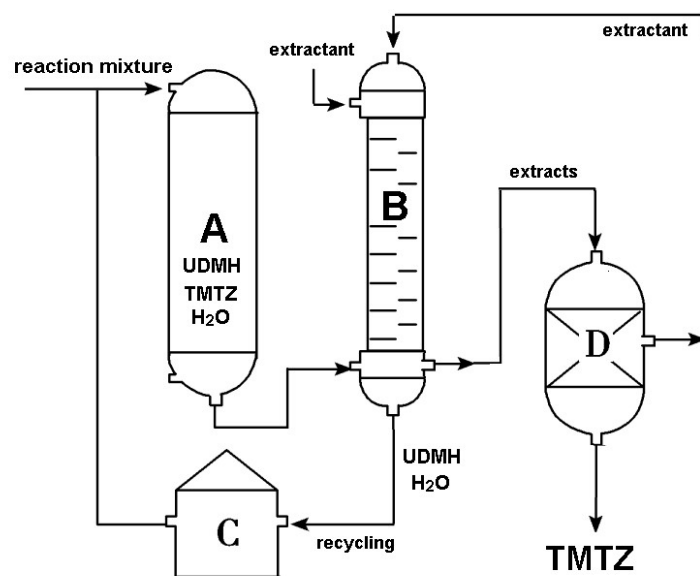


Fig. S9 Flowsheet of the continuous production process of TMTZ obtained from UDMH electrochemical oxidation: A electrochemical oxidation; B extraction; C pump; D rectification.