IOCM 2025 Conference

The 4th International Online Conference on Materials

3–6 November 2025 | Online

MDPI

# Stable Hydrazyl Radicals as Redox Active Materials

**Petre IONITA**

**University of Bucharest, Faculty of Chemistry, 90 Panduri, Bucharest, Romania**

## INTRODUCTION & AIM

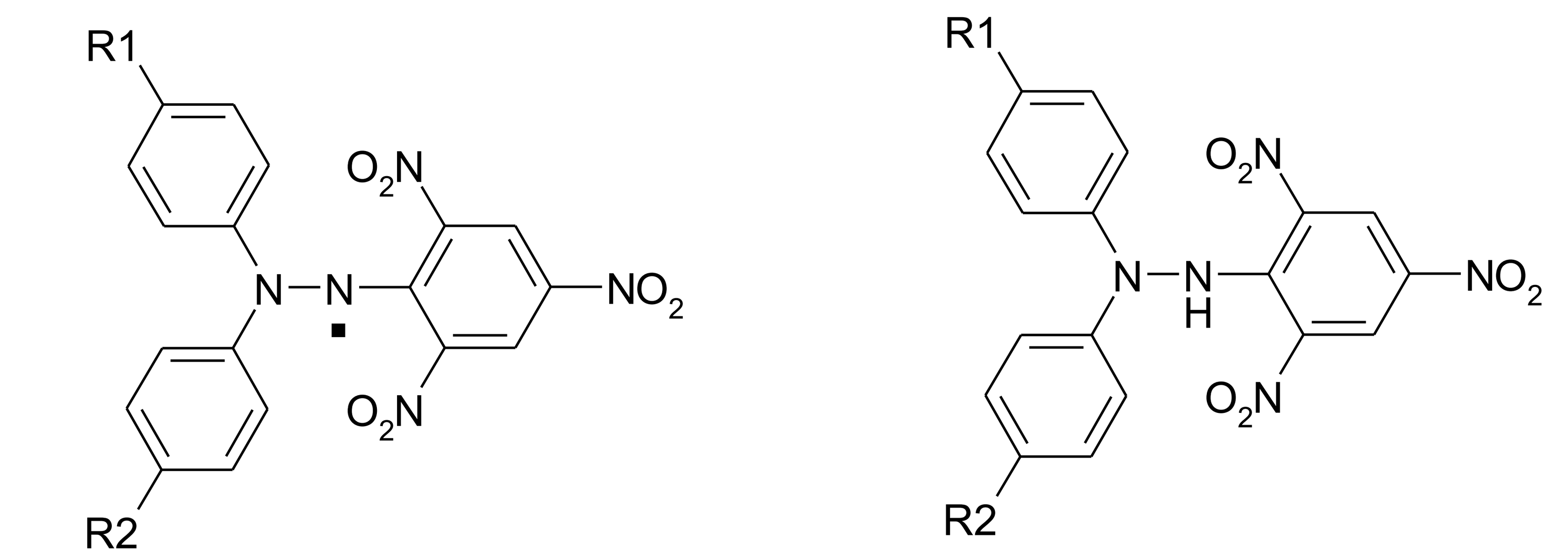
- Stable organic compounds with unpaired electrons (open-shell molecules) are known as free radicals, and usually they possess fascinating and unique properties, the most important being their redox behaviour.
- Stable hydrazyl free radicals are ideal redox species for such new batteries. To this moment, the well-known DPPH free radical (2,2-diphenyl-1-picrylhydrazyl) was tested as redox mediator in a lithium-graphene battery [1].
- Organic radical batteries promise an improvement on all characteristics of classical batteries, regarding freedom from rare metals, faster charging time, environmental friendliness, and so on.
- Stable hydrazyl free radicals are ideal redox species for such new batteries.

## METHOD

- This work was primarily focused on the synthesis and characterization of a large number of such stable hydrazyl (di)radicals, thus tailoring their redox properties, by chemical design.
- Structural characterization was performed by NMR, IR, UV-Vis, MS, (para)magnetic measurements (ESR, SQUID), and cyclic voltammetry, that allows the evaluation of the redox properties.

## RESULTS & DISCUSSION

- Structures of the DPPH free radical derivatives were confirmed by different means. Electrochemistry was performed for both stable and persistent free (di)radicals [2].
- As expected, stable radicals showed a full reversible redox process. The oxidation potential usually ranges in the domain 0.5-1.5 V, higher values being recorded for poly-nitrated radicals and diradicals.
- The bond dissociation energy of the -NH- group (hydrazine-hydrazyl) is around 70-90 kcal/mol. Further experiments are underway.




| | | | |
|---|---|---|---|
| R1 = R2 = H | $E^0$ = 0.30 V *vs.* SCE | R1 = R2 = H | $pK_a$ = 8.5 |
| R1 = H; R2 = $NO_2$ | $E^0$ = 0.49 V | R1 = H; R2 = $NO_2$ | $pK_a$ = 7.2 |
| R1 = R2 = $NO_2$ | $E^0$ = 0.60 V | R1 = R2 = $NO_2$ | $pK_a$ = 6.5 |

**Figure 1.** Typical structures of hydrazyls/hydrazines and their acid-base and redox characteristics.

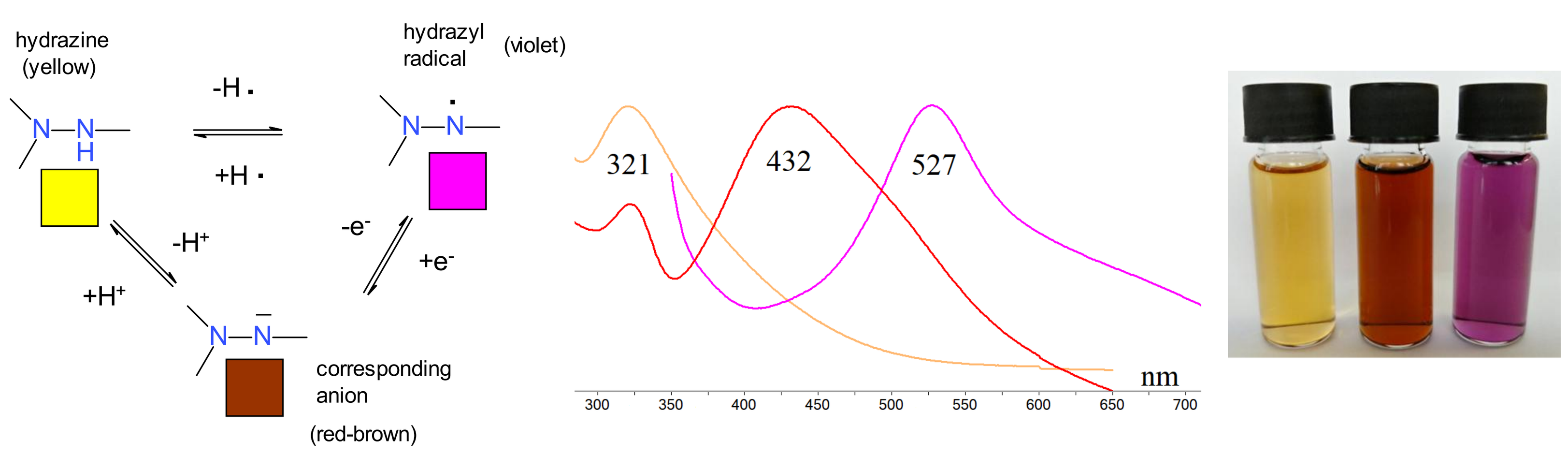



**Figure 2.** Each process is accompanied by colour changes.

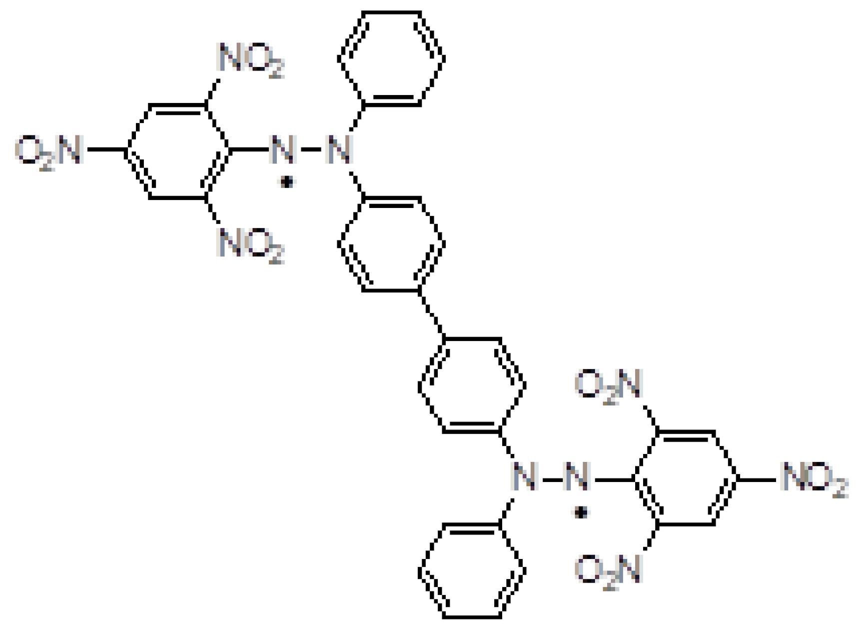



**Figure 3.** Structure of the DPPH-diradical.

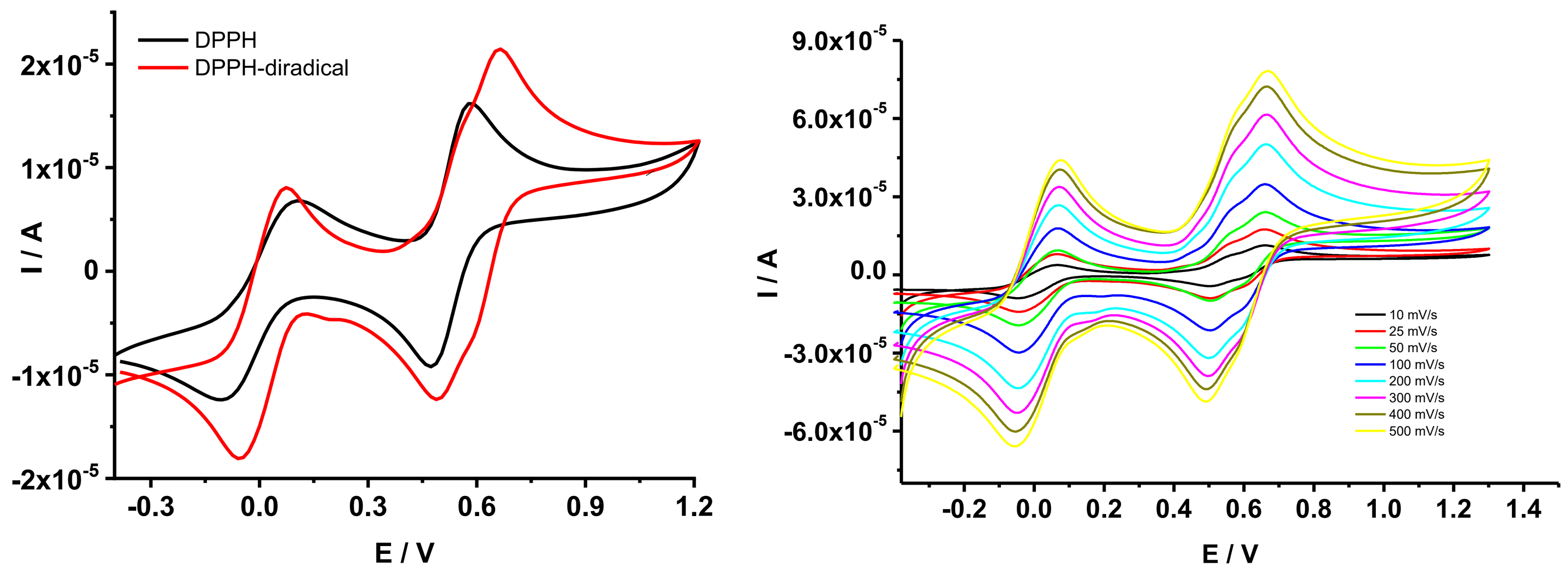



**Figure 4.** Typical CVs of hydrazyls: left) DPPH and DPPH-diradical; right) DPPH-diradical at different CV speeds.

- Both oxidation and reduction processes were reversible.
- Different compounds have different properties, thus allowing a design by synthesis for specific required characteristics.
- Diradicals can swich thermally from singlet state to triplet state [2].

**Table 1.** Electrochemical parameters for DPPH and DPPH-diradical.

| | $I_{a1}$ (μA) | $E_{a1}$ (V) | $I_{a2}$ (μA) | $E_{a2}$ (V) | $I_{c1}$ (μA) | $E_{c1}$ (V) | $I_{c2}$ (μA) | $E_{c2}$ (V) | ΔEp1 (V) | ΔEp2 (V) | $I_a/I$ (1) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| DPPH | 8.27 | 0.102 | 10.98 | 0.620 | -7.23 | -0.101 | 10.82 | 0.478 | 0.203 | 0.142 | 1.1 |
| DPPH-diradical | 12.86 | 0.073 | 15.89 | 0.662 | -12.02 | -0.050 | -9.25 | 0.497 | 0.123 | 0.165 | 1.0 |

- Stable hydrazyl radicals are proved as possible redox mediators for organic batteries.
- Besides, full-organic batteries can be envisaged.

## ACKNOWLEDGEMENTS

UEFISCDI support from the project number PN-IV-P1-PCE2023-0267 is gratefully recognized.

## CONCLUSION

- The use of stable hydrazyl radicals in organic batteries might be an important step towards a new technology for generation and storage of electrical energy.
- New encouraging experiments are undergoing, showing applicative interests.

## REFERENCES

[1]. Boosting the electrochemical performance of Li-O2 batteries with DPPH redox mediator and graphene-luteolin-protected lithium anode. Bai, W.L.; Zhang, Z.; Chen, X.; Wei, X.; Zhang, Q.; Xu, Z.X.; Liu, Y.S.; Chang, B.; Wang, K.X.; Chen, J.S. Energy Storage Mater., 2020, 31, 373-381. DOI: 10.1016/j.ensm.2020.06.036

[2]. Dimer of the DPPH stable radical. A. Dobre, C. Lete, N. Iacob, V. Kuncser, A. Mădălan, G. Ionita, M. Harada, Y. Kitagawa, P. Ionita. ACS Omega, 2025, 10, 36662-36671. DOI: 10.1021/acsomega.5c05905