Hydrogenation of Hexaazatrinaphthylene (HATN) in alcohols with visible light

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Introduction

HATN (Scheme 1) is an electron poor system with high electron affinity.[1] Its derivatives are being intensively investigated as desirable alternatives for sustainable lithium-ion battery electrodes that offer high capacity and long-term cyclic stability.[2-5] A successive six-fold lithiation has been reported for HATN in the solid state.[2] A photochemical process was observed for HATN in methanol.[6] In this work we check if Proton Coupled Electron Transfer may lead to hydrogenation of HATN in alcohols and water:

$$HATN + CH_3OH + h\nu \rightarrow HATN\text{-}H\bullet + CH_3O\bullet \qquad (1)$$

$$HATN + H_2O + h\nu \rightarrow HATN\text{-}H\bullet + OH\bullet \qquad (2)$$

HATN in alcohols

Fig. 1. Colorization of HATN solution in methanol upon irradiation with 405 nm laser: solution before (left) and after 15 minutes of photoexcitation at 405 nm (right).

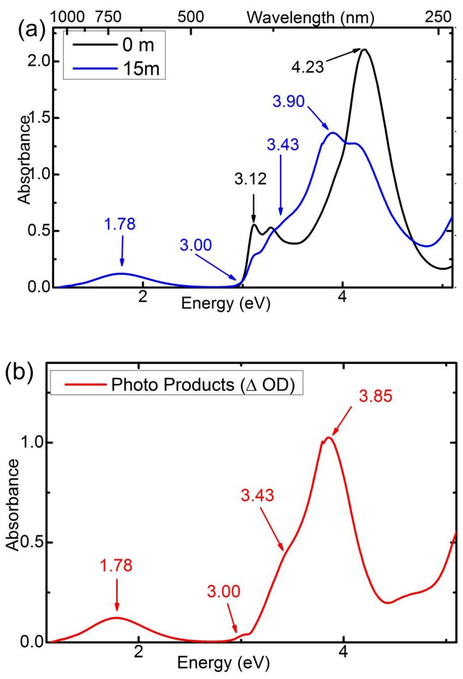


Fig. 2. (a) Absorption of HATN solution in methanol before (black line) and after 15 minutes of phototoirradiation with a 405 nm laser (blue line), (b) absorption spectrum of photoproducts – the difference between "after-" and "before irradiation" absorption spectra of panel (a). Numbers denote band maxima in electronvolts.

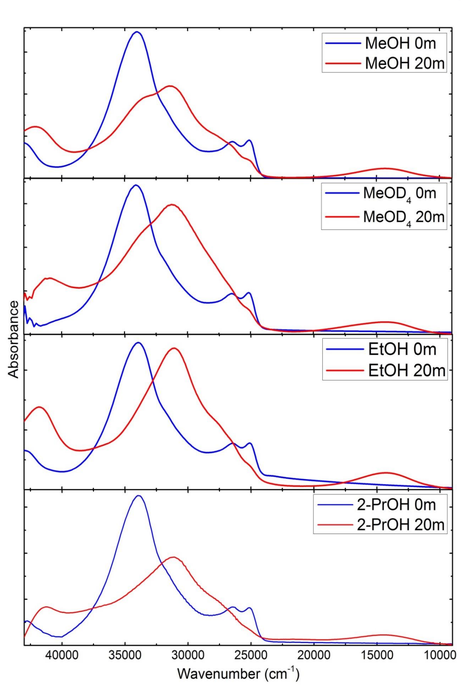
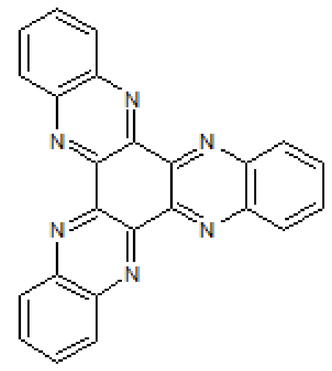


Fig. 3. Absorption spectra of HATN in alcohols before (blue) and after 20 minutes irradiation with 405 nm laser (red line).



Scheme 1. Structure of HATN.

HATN in water

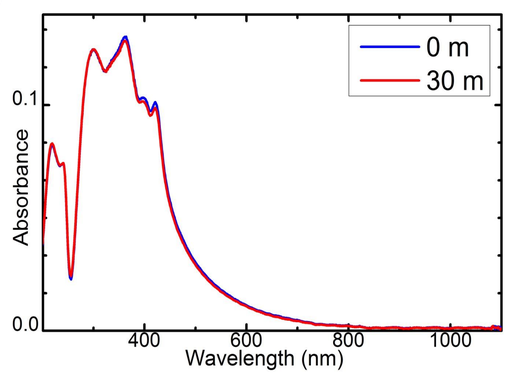


Fig. 4.. Absorption spectra of HATN in water before (blue) and after 30 minutes irradiation with 405 nm laser (red line). HATN in water forms suspension and spectrum contains an additional band at 362 nm assigned to absorption of the H aggregates and a long tail resulting from Rayleigh scattering.

Optical, EPR, NMR and MS detection of photoproducts

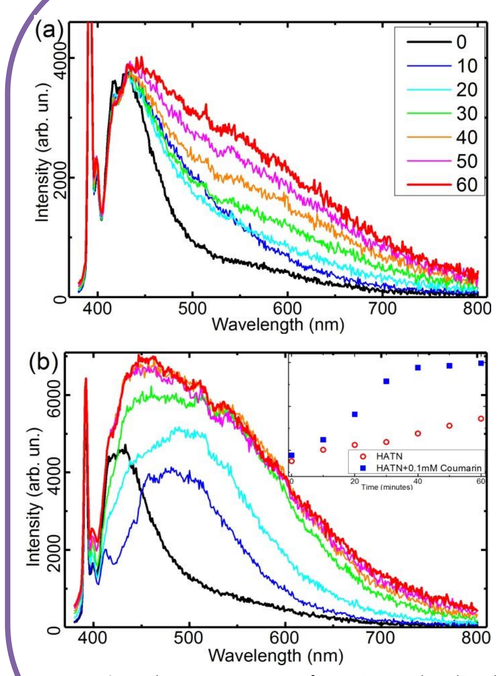


Fig. 5. Fluorescence spectra of HATN in a methanol irradiated with a 405 nm laser and recorded with 10 minutes intervals (a), same for HATN with 0.1 mM coumarin in methanol (b). Spectra recorded with 340 nm excitation.

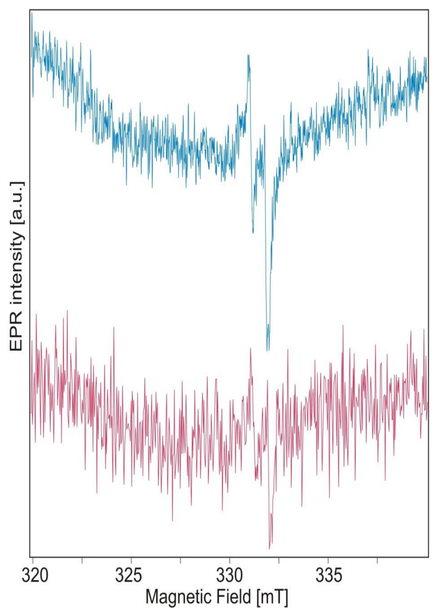


Fig. 6. EPR spectra of HATN in methanol before (red) and after (blue line) photorirradiation with 405 nm laser. Spectra recorded at 100 K, photoirradiation conducted at room temperature. The spectrum of the photoirradiated solution (top) contains the signal of the ½ spin with hyperfine splitting A = 0.75 mT and g-factor g = 2.0044, proving the creation of radicals.

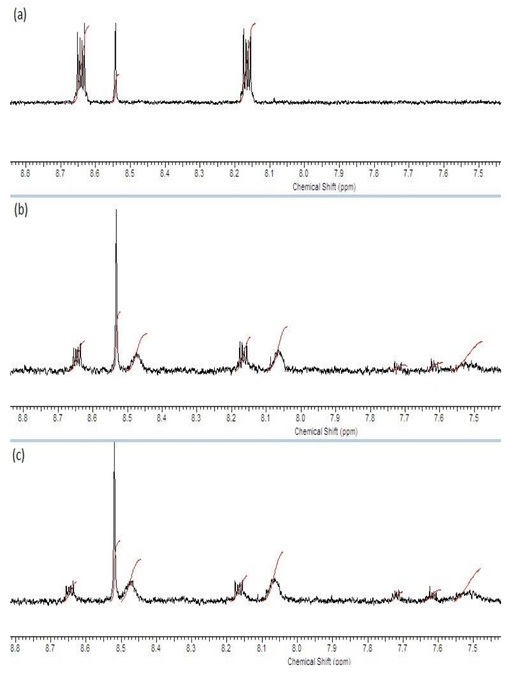
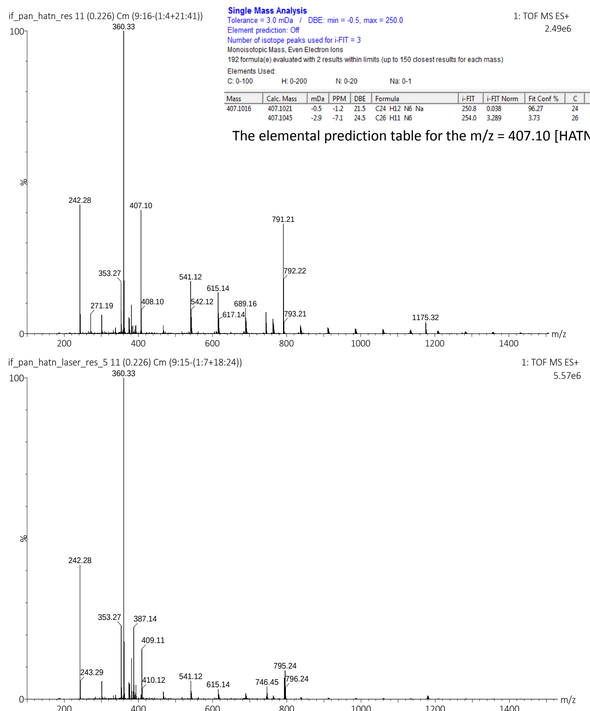
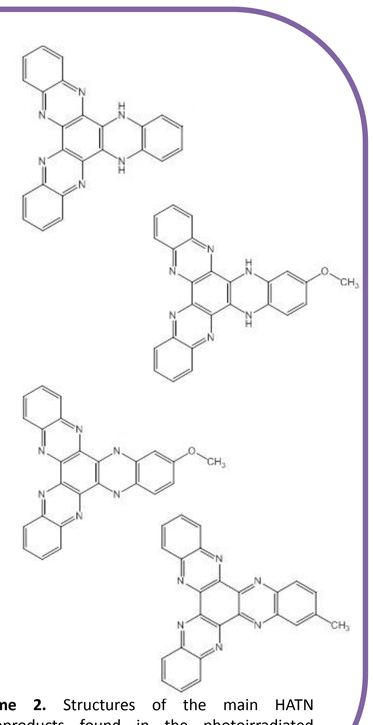


Fig. 7. NMR spectral changes of HATN in CD_3OD (a) before irradiation, (b) after 5 minutes and (c) after 10 minutes of irradiation with 405 nm laser. The vertical scale is different for (a), (b) and (c).



Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	Na
407.1016	407.1021	-0.5	-1.2	21.5	C24 H12 N6 Na	250.8	0.038	96.27	24	12	6	1
	407.1045	-2.9	-7.1	24.5	C26 H11 N6	254.0	3.289	3.73	26	11	6	

Fig. 8. The mass spectrum of HATN in methanol before (top) and after (bottom panel) 405 nm laser 10minutes irradiation, positive polarity.



Scheme 2. Structures of the main HATN photoproducts found in the photoirradiated methanol solution with high resolution mass spectrometer. Positions of the attached atoms and groups are ambiguous.

Theoretical exploration

Table 1. Vertical excitation energy (in eV) and oscillator strength (in parentheses) of the lowest excited states of HATN and its complexes with water and methanol molecules determined with the ADC(2)/cc-pVDZ method at the MP2/cc-pVDZ equilibrium geometry of the ground state.

State	HATN	HATN-H_2O	HATN-MeOH
$^3A(\pi\pi^*)$	2.80	2.78	2.77
$^3E(\pi\pi^*)$	2.98	2.95 3.96	2.94 2.95
$^3E(n\pi^*)$	2.99	3.01 3.02	3.01 3.01
$^3A(n\pi^*)$	3.08	3.12	3.11
$^1E(n\pi^*)$	3.41(0.0)	3.43(0.0) 3.43(0.0)	3.42(0.0) 3.43(0.0)
$^1A(n\pi^*)$	3.50(0.0)	3.53(0.005)	3.52(0.005)
$^1A(\pi\pi^*)$	3.70(0.0)	3.70(0.072)	3.69(0.066)
$^1E(\pi\pi^*)$	3.71(0.422)	3.67(0.103) 3.68(0.217)	3.66(0.101) 3.67(0.217)

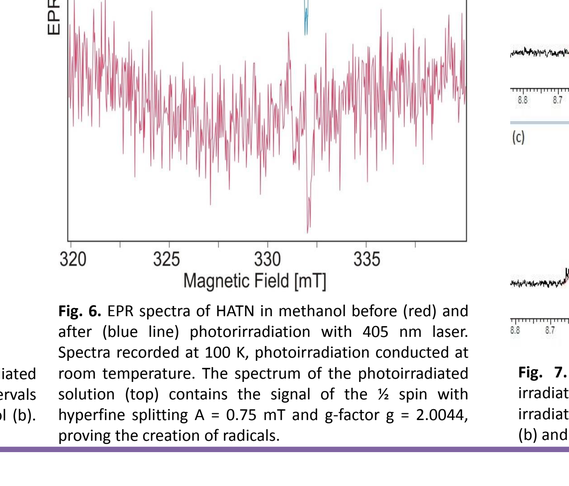


Fig. 9 PE profiles of relaxed scan for H-atom transfer from methanol to HATN computed along the OH distance of MeOH in different electronically excited states of the complex: $^1\pi\pi^*$- blue squares, $^1n\pi^*$- green diamonds, $^3\pi\pi^*$- violet triangles, $^3n\pi^*$- red triangles, connected by solid lines. Vertical energy profile of the ground state (circles connected by dashed lines) was computed along the relaxed scan in a given electronic state as encoded by color.

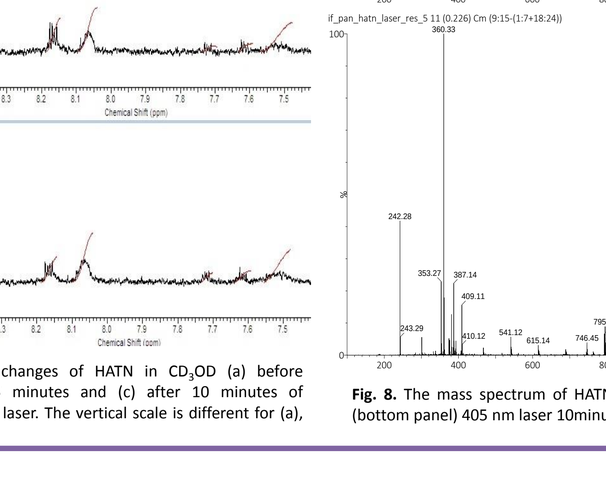


Fig. 10 Figure PE profiles of relaxed scan for H-atom transfer from water to HATN computed along the OH distance of H_2O in different electronic excited states of the complex: $^1\pi\pi^*$- blue squares, $^1n\pi^*$- green diamonds, $^3\pi\pi^*$- violet triangles, $^3n\pi^*$- red triangles connected by solid lines. Vertical energy profile of the ground state (circles connected by dashed lines) was computed along the relaxed scan in a given electronic state as encoded by color.

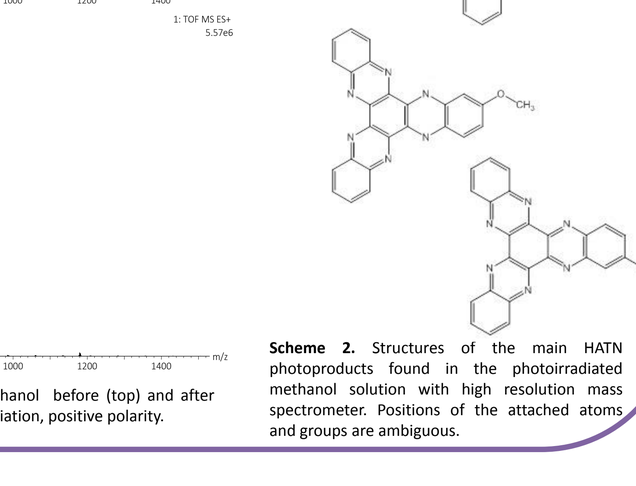


Fig. 11 Simulated absorption spectra of HATN-2H computed with TD-DFT (red), ADC(2) (blue), CC2 (green) methods. The computed stick spectra were convoluted with Gaussian function of 0.25 eV FWHM.

References:

[1] Shao, J.; Chang, J. and Chi, V., *Org. Biomol. Chem.*, **2012**, *10*, 7045–7052.
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Conclusions:

- Photochemical hydrogenation of HATN in alcohols is possible with visible violet light.
- In water the energetic condition for intermolecular PCET reaction is unfavorable.
- The excited state hydrogen transfer leads to stable di-hydrogenated HATN monomers.
- The photochemical hydrogenation occurs also in small aggregates, were up to two H atoms can be retained per HATN molecule.