



NOVEL SYNTHETIC APPROACHES TOWARDS HEXAAZATRIPHENYLENE (HAT) DERIVATIVES



María Mar Ramos^a, Rafael Juárez^{a,b}, José Luis Segura^b

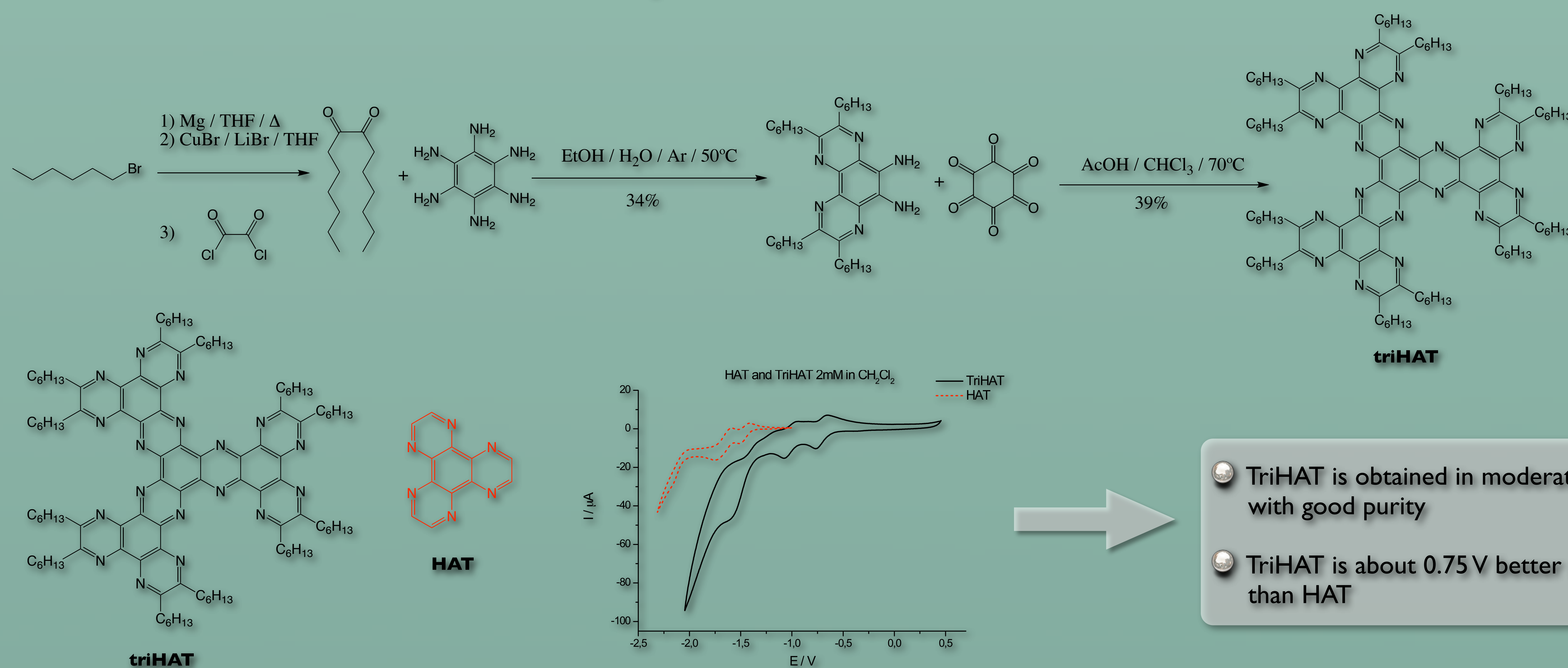
^a Universidad Rey Juan Carlos, c/ Tulipán s/n, Móstoles, España

^b Universidad Complutense de Madrid, Av. Complutense s/n, Madrid, España

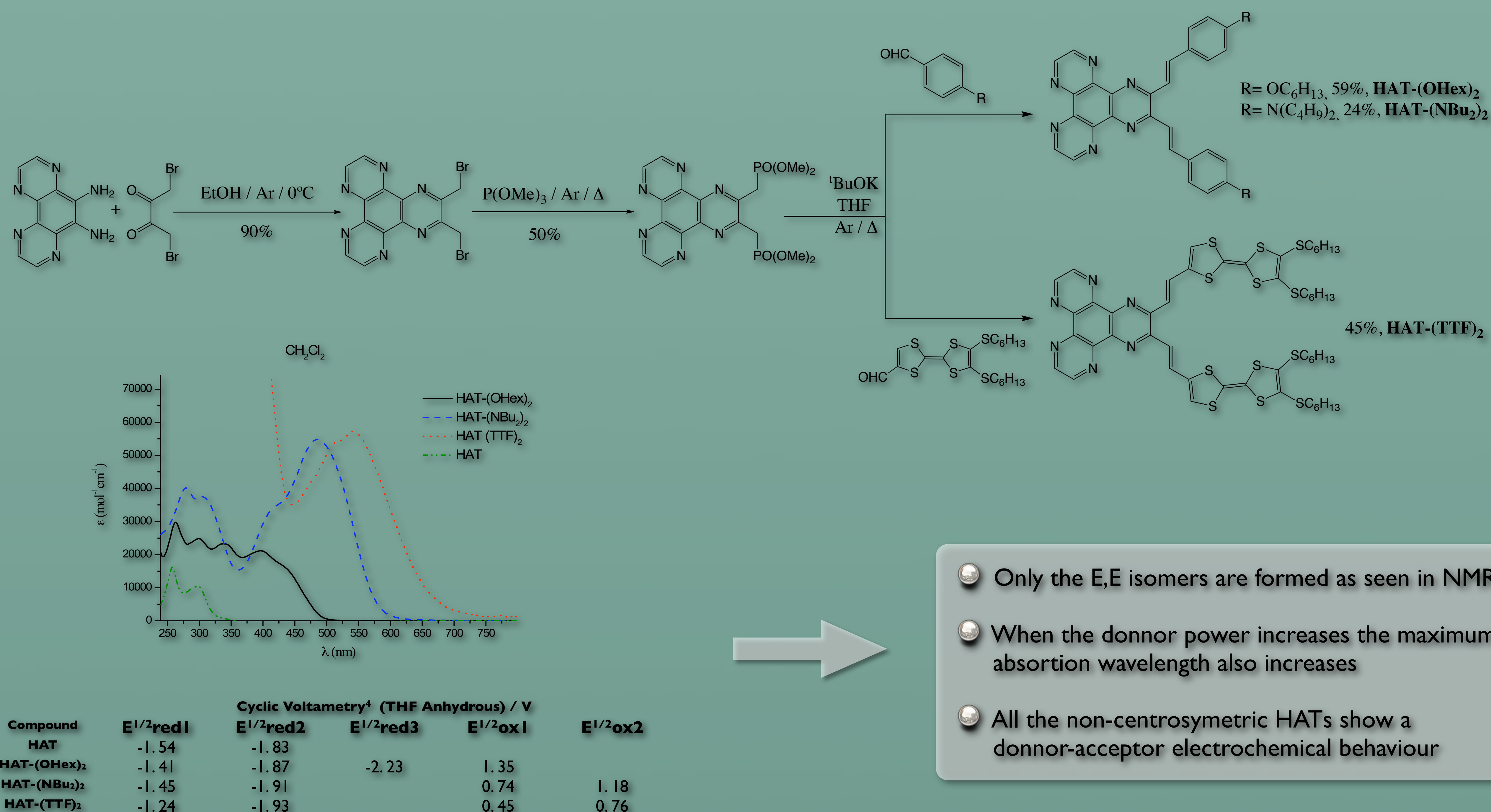
Contact: mariamar.ramos@urjc.es; segura@quim.ucm.es

Summary: Large two-dimensional molecules with extended π -systems are subject of increasing interest as a consequence of their technological applications. In particular, hexaazatriphenylene (HAT) derivatives, present a great interest due to the influence of heteroatoms on the electronic nature without modifying the structure. HAT derivatives have recently attracted attention as materials for organic electronic applications¹ and depending on the choice of substituent can have a variety of applications (discotic liquid-crystals, n-type semiconducting, magnetic materials or fluorescent dyes).² Whereas HATs carrying six identical substituents are well known following different synthetic approaches, the synthesis of non-centrosymmetric HAT derivatives is still quite rare. In our working group we are centered in two main routes for affording HAT derivatives. One route affords a variety of symmetrical HAT derivatives including HAT condensed systems. On the other hand, we have also synthesized non-centrosymmetric π -conjugated donor-acceptor molecules bearing a HAT core and donor groups in the periphery.³ In this communication we present a new soluble π -deficient derivative which consists of three HAT molecules condensed around a central aromatic core so we have named it triHAT. We have found triHAT to be 0.75 V better acceptor than HAT in itself. We also present a new synthetic route in order to obtain non-centrosymmetric π -conjugated donor-acceptor molecules bearing a HAT core and donor groups in the periphery. This synthesis paves the way for further conjugated donor-acceptor derivatives of HAT.

TriHAT Synthesis and Redox⁴ Behaviour



Non-centrosymmetric HAT Synthesis, UV-Vis Absorption Spectroscopy and Redox⁴ Behaviour



Acknowledgements:

This work has been supported by the MCyT of Spain (Project CTQ2007-60459), a Comunidad de Madrid-Universidad Complutense joint project (CCG07-UCM/PPQ-2126, Group Nr.: 910759). R. Juárez is indebted to Universidad Rey Juan Carlos for a doctoral fellowship.

References:

- Carbon-Rich Compounds; Haley, M. M., Tylkinski, Eds.; Wiley, VCH: Weinheim, 2006; Watson, M. D.; Fehetenkötten, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.
- (a) Pieterse, K.; van Hal, P.A.; Kleppinger, R.; Vekemans, J.A.J.M.; Janssen, R.A.; Meijer, E.V. *Chem. Mater.* **2001**, *13*, 2675-2679; (b) Ishi-I, T.; Yaguna, K.; Kuwahara, R.; Taguri, Y.; Mataka, S. *Org. Lett.* **2006**, *8*(4), 585-588.
- Juárez, R.; Ramos, M. M.; Segura, J. L. *Tetrahedron Letters*, **2007**, *48*, 8829.
- All measurements were carried out in anhydrous solvents solutions using: concentrations of 0.1M for Hexafluorophosphate of Tributylammonium and 2mM for the samples, Pt working and auxiliary electrodes, Ag / Ag⁺ reference electrode. Scan rate 100mV/s. All values are referenced to the Fc / Fc⁺ pair.