Hole-Transporting Materials for solar cells. Quantum chemistry study

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Abstract

This work is devoted to quantum chemistry study of Tröger's base (TB) derivatives, synthesised for solar cells. TB with enamine-linked diphenyl branches could be titled as the most promising hole-transporting materials (HTM). For several derivatives, ground state geometry was established, and electronic excitation behaviour was estimated. Analyse of molecular charge redistribution allows concluding the significance of TB: dynamics between *switch-on*, *switch-off* states could be realised by manipulating HOMO and LUMO.

Keywords: Tröger's base, TB; hole-transporting materials, HTM

1 Introduction

Tröger's base (TB) represents the nonplanar compound with a tetracyclic structure - bicyclic aliphatic unit fused with two aromatic rings as presented in Figure 1. Due to V-shaped structure, TB and its analogues are applicable as ligands with well-expressed functional possibilities. Presence of interactive groups at functional place *R* allows to start a host–guest chemistry interaction, which occurs between the TB and other molecules [1]. TB could be used as the functional core for synthesis of materials which exhibit hole-transporting (HT) properties and high charge mobility [2]. Chromophore carrying analogues of the TB have displayed unique NLO properties and can be used as very stable molecular switches [3].

This work is devoted for quantum-chemistry study of structure and electronic properties of most-promising hole-transporting materials (HTM) based on TB [4]. Several structures HTM1–HTM3 containing TB with enamine-linked diphenyl branches are presented and discussed – see Figure 2.

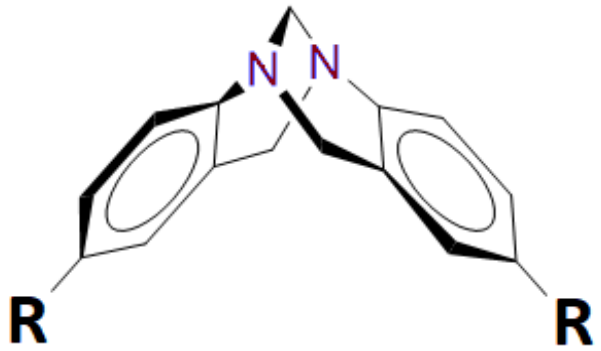

Figure 1 Tröger's base (TB)

2 Overview

Quantum chemistry study was provided using *Gaussian-09* package [5]. Ground state geometry optimization was done using density functional method B3LYP and 6-31G(d) base with polarization functions. PCM model was used for including the surrounding effect (in that case THF). According to geometry optimization data, it was established that central methanodiazocine unit orientates the aromatic rings in a nearly perpendicular fashion, making TB a rather rigid V-shaped molecule, its angular orientation of aromatic rings creating a hydrophobic cavity. Also, additional fragments such as methyl or methoxy groups increase the chaoticity within the enamine-linked diphenyl branches to shorten the length of π-conjugation within them.

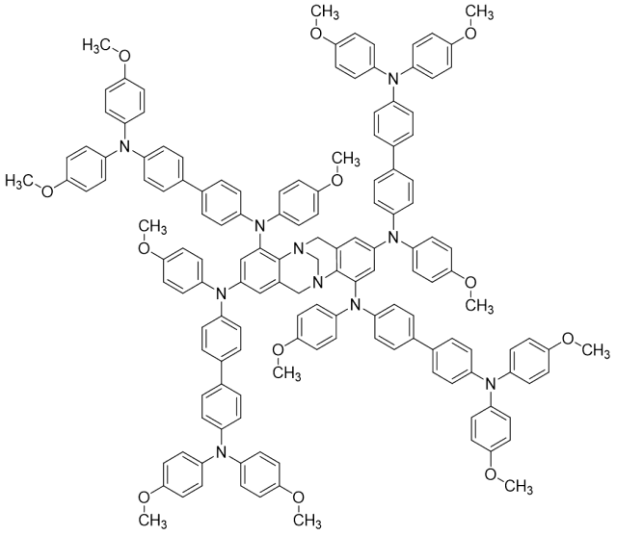

Figure 2 HTM3 structure based on TB with enamine-linked diphenyl branches

Electronic excitations were established using *Gaussian-09* package be means of semiempirical TD method (for singlets only) in the framework of B3LYP/6-31G(d). Excitation energies, corresponding wavelengths and oscillator strengths were calculated for low lying spectroscopic states $S_0 \rightarrow S_1$, …, $S_0 \rightarrow S_6$.

Generally, for HTM1-HTM3 structures, the singlet S_1 electronic state could be populated by means of two one-particle transitions, nextHOMO→LUMO and HOMO→LUMO, favouring charge delocalization in the left fragment (more chaotic). In this case, the TB fragment plays an important role as a bridge fragment, containing two nitrogen atoms, built-up from two related hexagons consisting of carbon atoms and nitrogen atoms connected by a one-valence junction. Owing to the spatial orientation of hexagons having a circa 105 deg angle, a π-conjugated system occurs along the entire molecule, from the left to the right fragment.

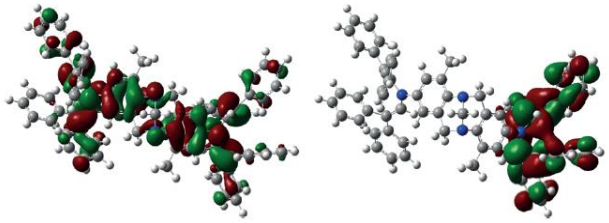

Figure 3 HTM1 structure. Electronic transition $S_0 \rightarrow S_1$. Charge redistribution process by populating the first excited electronic state between HOMO (left) and LUMO (right)

Figure 3 shows a typical charge redistribution process for HTM1 structure at electronic transition $S_0 \rightarrow S_1$. By populating the first excited electronic state S_1, the first and second central nitrogen atoms from TB are associated to the π-conjugated systems, expanded by enamine-linked diphenyl branches, on the left and right sides, respectively. A separation line goes through the central structural peak represented by the $–CH_2$ group, connecting two nitrogen atoms. Owing to a nonstandard off-plane angle of fragment orientation (105 deg), a π-conjugated system occurs along the molecule. From classical molecular electronics perspective, TB acts as a switch (HOMO distribution corresponds to switch-on, LUMO to switch-off). After excitation, charge localization is limited by a nitrogen in the right enamine-linked fragment, indicating the establishment of a radical cation [2].

3 Conclusion

TB with enamine-linked diphenyl branches could be titled as the most promising hole-transporting materials (HTM). For several derivatives, ground state geometry was established, and electronic excitation behaviour was estimated. Analyse of molecular charge redistribution allows concluding the significance of TB: dynamics between *switch-on*, *switch-off* states could be realised by manipulating HOMO and LUMO.

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