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Novel push–pull dendrons with high excited state dipole moments. Synthesis and theoretical analysis of unusual “branched electron distribution”

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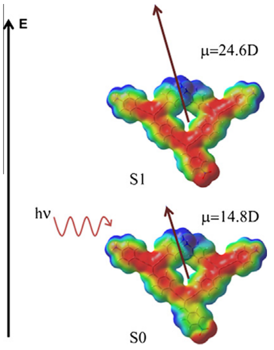
HIGHLIGHTS

- Novel push–pull dendrons with high excited state dipole moments were synthesized.
- The rigidity and high delocalization of dendrons promote charge transfer mechanisms.
- Delocalized push–pull dendron (8) exhibits an unusual branched electron distribution.
- High excited state dipole moments can be related to efficient photovoltaic processes.
- Solvatochromic method is a useful tool to estimate dipole moments in excited state.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of novel highly delocalized push–pull dendrons is described. A modified protocol to conventional C—C coupling reaction was used with moderate yields. The excited state dipole moments of synthesized dendrons were estimated by the solvatochromic model using the E_T^N polarity scale. In case of dendron of second generation with donor–acceptor groups, values around 23 D are obtained, denoting an efficient charge separation crucial in photovoltaic processes. From the theoretical analysis, there is a clear evidence of highly efficient electron delocalization in case of push–pull dendrons. The chosen theoretical model (M05-2X/cc-pVDZ) to describe the electronic behavior of the molecules under study was very precise in the estimation of dipole moments in excited state, with differences of 0.5–2.2 D, compared with the values obtained by the solvatochromic model.

Introduction

In the area of materials science, efforts have been made to propose new materials able to mediate the conversion of energy from sunlight to be used in optoelectronic devices such as solar cells, extensively developed during the past 30 years. Organic materials have found wide acceptance in this field due to their low cost, flexibility and easy processing. The molecular systems known as push–pull or excitonic materials are promising as organic photovoltaics (OPVs) [1–3], and have been explored in different molecular architectures, including the non-conventional highly branched dendritic framework [4], resulting in potential organic materials for efficient photogeneration and separation of charges [5–8]. Previously in our group were theoretically studied a set of dendritic molecules (and their linear counterparts), demonstrating that

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dendritic architecture of push–pull molecules favors the charge transfer in the excited state compared to linear molecules [9]. The dissociation of photogenerated electron–hole pairs (excitons) into free charge carriers is crucial in photovoltaic processes and the excited state dipole moment (μ^*) is the parameter that accounts for this phenomenon [10], thus the knowledge of μ^* may be directly used to establish structure–property relationships related to the performance of OPV materials.

Among the experimental techniques to determine μ^*, the solvatochromic methods have been extensively used due to their good compromise between facility, low cost and precision [11,12]. Solvatochromic models can be categorized into those considering specific solvent effects (hydrogen bond interactions) [13,14], and those considering nonspecifically the solvent effects, assuming instead that carefully selected probe molecules (generally dyes) with well-understood and strongly solvent-dependent spectral absorptions may serve as suitable models to be correlated with a variety of molecules under investigation. In this sense, a variety of empirical solvent polarity scales have been developed [15,16]. Particularly the E_T^N dimensionless scale of solvent polarity [17], based on the solvatochromism of pyridinium N-phenolate betaine dyes, has been useful to correlate solvatochromism of Stokes shifts to estimate excited state dipole moments in a reliable way [18].

Taking as starting point our earlier theoretical study, herein we report the synthesis of novel push–pull dendrons, and the estimation of excited state dipole moments by the solvatochromic model involving the E_T^N polarity scale, in order to relate this parameter with the dendritic architecture and the potential performance of these organic compounds as photovoltaic candidates. Additionally the electron density distribution, by molecular orbitals and electrostatic potential maps, was used to rationalize the charge transfer processes on these branched molecules.

Results and discussion

Synthesis

Following the synthetic route shown in Fig. 1, fully conjugated dendrons (5) and (8) with donor–acceptor groups were obtained, as well as dendrons (6) and (9) with two different electron withdrawal groups, $-NO_2$ and $-COH$, in the focal point and in the periphery respectively.

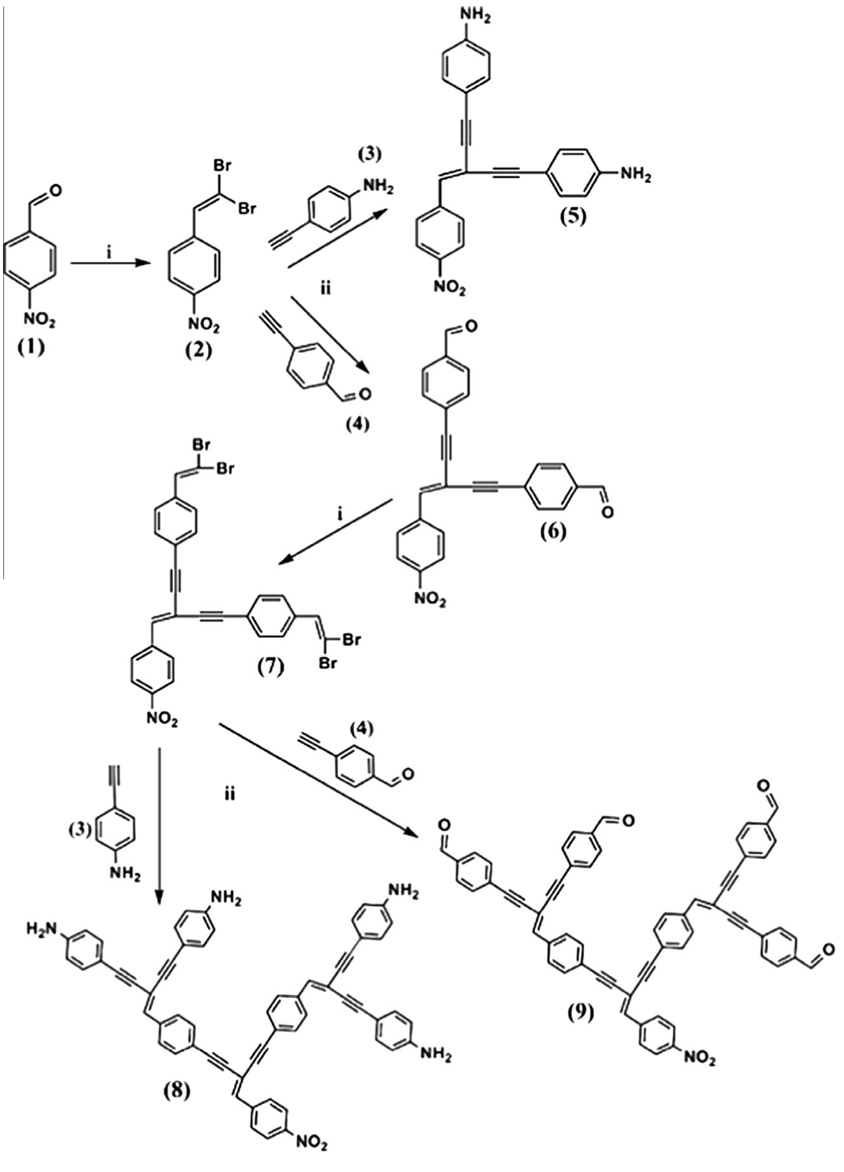

Fig. 1. Synthetic route to obtain fully conjugated dendrons. (i) $CBr_4/P(Ph)_3$, CH_2Cl_2 (Wittig reaction); (ii) $Pd(OAc)_2/NEt_3$, PEG-200 (C—C coupling reaction).