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Carbon dendron nano-chains with π-extended conjugation based on end-capped *N*,*N*-dimethylamino in linear 1,4-phenylethynyl or in 1,5-naphthylethynyl subunits: fluorescence analysis

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Abstract—The synthesis of dendrons with the end-capped 5-(*N*,*N*-dimethylamino)naphthyl-1-ethynyl unit connected to conjugated naphthylethynyl or *p*-phenylethynyl chains, as the branches of the 1,3,5-substituted benzene core, have been undertaken by heterocoupling reaction between 1,3,5-triiodobenzene and the convenient end-capped 5-(*N*,*N*-dimethylamino)naphthylacetylene or 5-(*N*,*N*-dimethylamino)naphthylethynylphenylacetylene in the presence of the palladium–copper catalyst system, in excellent yields. The influence of the alternating naphthylethynyl–phenylethynyl chains on the fluorescence emission radiation, in the dendron structures, has been analyzed.

1. Introduction

Hyperbranched polymers and dendrimers are highly branched macromolecules that have received considerable attention.[1–5] Dendrimers are synthesized by multistep reactions requiring tedious purification, whereas hyperbranched polymers are prepared by one-step polymerization resulting in less regular structures. An undesirable feature of the one-step polymerization is the loss of control in molecular weight, accompanied by broad molecular weight distributions[6] and possible intramolecular cyclization.[7]

The convergent method for synthesizing dendrons and dendrimers had been reported by Hawker and Fréchet,[8] and this appeared to be the best method for making well-defined structures.

The area of highly conjugated, all-carbon and carbon-rich macromolecules continues to be of intense attention.[9] The synthesis and characterization of nanometer-sized conjugated molecules of precise length and constitution are of wide-spread interest, which is due to their inherent synthetic flexibility which permits the design of molecular architectures with important properties.[10,11] Molecules showing π-extended conjugation, in general, can present electroconductive, magnetic and optical properties.[12] A variety of potential applications such as artificial photosynthesis,[13] photocatalysis,[14] molecular photovoltaic cells,[15] molecular informatics,[16] and optoelectronic devices,[17,18] are beginning to emerge from this new field of research.

Conjugated systems integrated by 1,4-diethynyl or 1,3,5-triethynylphenyl units have been used in the preparation of aromatic oligomers bearing multiple ethynyl groups that exhibit electroluminescence properties,[19] poly(phenylvinylene) with fluorescence properties as well as dendrimers[20] with poly(yne) chain.[21] The triple bond play the role of a wire while the polyaromatic system behaves as an energy relay subunit.

We now report the controlled synthesis of a novel family of rigid conjugated dendron nanostructures with a controlled geometry and the fluorescence properties.

2. Results and discussion

The syntheses of the end-capped 5-(*N*,*N*-dimethylamino)-naphthylacetylenes (**1**, **2** and **3**) designed as the branches of the 1,3,5-benzene dendron structures were carried out by the heterocoupling between the terminal naphthylacetylene and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol,[22] in presence of $PdCl_2(PPh_3)_2$ and Cu_2I_2 catalyst system, in NEt_3, Scheme 1.

Compound **1** was obtained by heterocoupling reaction between 5-iodo-*N*,*N*-dimethylnaphthalen-1-amine and

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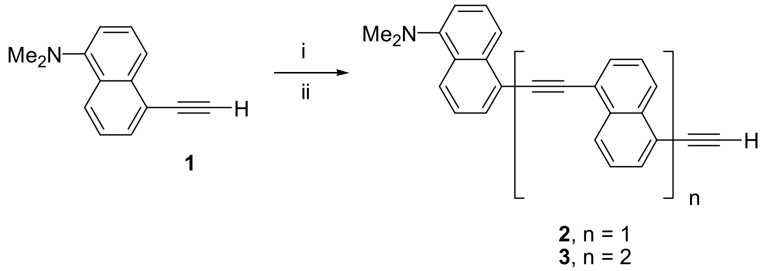

Scheme 1. (i) $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3, 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol. (ii) NaOH, toluene, at the reflux temperature.

2-methyl-3-butyn-2-ol in NEt_3, catalyzed by the palladium–copper system to give the propargyl intermediate, which by treatment with a catalytic amount of powdered NaOH in toluene, at the reflux temperature, gives **1** as a dark amber solid, in practically quantitative yield.

The naphthylacetylene homologue **2** was satisfactory obtained by the heterocoupling between the terminal acetylene **1** and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol in NEt_3, catalyzed by the palladium–copper system, under a rigorous carbon dioxide atmosphere,[23] to give the propargyl intermediate, which by treatment with a catalytic amount of powdered NaOH in toluene at the reflux temperature gives **2**, as a yellow solid, in practically quantitative yield. Under the palladium catalytic conditions, compound **1** was really sensitive to the homocoupling reaction to give the 1,3-diyne derivative, which was avoided by use of a compatible carbon dioxide atmosphere.[23]

Compound **3** was obtained by the heterocoupling between the terminal acetylene **2** and 4-(5-iodo-1-naphthyl)-2-methyl-3-butyn-2-ol, in NEt_3 under argon atmosphere, catalyzed by the palladium–copper system, giving the propargyl intermediate, which by catalytic treatment with powdered NaOH, in toluene at the reflux temperature affords **3** in quantitative yield.

The end-capped 5-(*N*,*N*-dimethylamino)naphthylacetylenes (**1**–**3**) show fluorescence emission spectra with an important quantum yield in dichloromethane, Table 1.

The analysis of the fluorescence emission spectra allows to some remarkable facts: (i) compounds **1** and **2** show only a broad emission band while **3** shows two bands; (ii) the emission bands of the compound **2** and the first band of **3** show a normal Stokes shift for conjugated naphthalene rings, while **1** and the second band of **3** show a large anomalous Stokes shift; (iii) the fluorescence quantum yields are considerable though a significant slight decreasing for compound **2**. These dual fluorescence and fast intramolecular charge transfer (ICT) effect were observed in *N*,*N*-dialkylaminophenyl[24] or naphthyl[25] derivatives.

The end-capped 5-(*N*,*N*-dimethylamino)naphthalenes connecting with *p*-phenylethynyl chains as **5** and **7** were designed as the branches of the 1,3,5-benzene dendron structures. The synthesis was carried out by the heterocoupling between the appropriate terminal acetylene and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol,[26] Scheme 2.

Thus, 5-[(4-ethynyl-1-phenyl)ethynyl]-*N*,*N*-dimethylnaphthalen-1-amine (**5**) was obtained in excellent yield,[27] by the heterocoupling between the terminal acetylene **1** and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol in NEt_3, in the presence of the palladium–copper system, under a rigorous carbon dioxide atmosphere,[23] to give 4-(4-{[5-(*N*,*N*-dimethylamino)-1-naphthyl]ethynyl}-1-phenyl)-2-methyl-3-butyn-2-ol (**4**), which was treated with a catalytic amount of powdered NaOH in toluene, at the reflux temperature.

The naphthylacetylene **7** was satisfactory obtained by the heterocoupling between the terminal acetylene **5** and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol in NEt_3, under argon atmosphere, catalyzed by the palladium–copper system, yielding the propargyl intermediate **6**, followed the treatment with a catalytic amount of powdered NaOH in toluene, at the reflux temperature.

The ultraviolet–visible absorption and fluorescence emission spectra of the end-capped 5-(*N*,*N*-dimethylamino)-naphthalenes with *p*-phenylethynyl chains (**5** and **7**) are summarized in Table 2.

In contrast with the naphthylacetylenes **1**, **2** and **3** the conjugated naphthylethynylphenyl acetylenes **5** and **7** show fluorescence emission radiation with a large anomalous Stokes shift and the quantum yields strongly decreases.

Table 1. UV–vis and fluorescence spectra of compounds **1**, **2** and **3**

Compound	UV–vis[a] (CH_2Cl_2) λ_{max}, nm	ε (M^{-1} cm^{-1})	F[b] (CH_2Cl_2) λ_{max}, nm	Φ_f
1	336	2200	463	0.63[c]
2	343	23,100	397	0.55[d]
3	363	26,600	398 and 414	0.65[d]

[a] At room temperature.

[b] At room temperature and $[c]\cong 10^{-8}$ M.

[c] Fluorescence quantum yield in dichloromethane relative to quinine sulfate in 1 N H_2SO_4.

[d] Fluorescence quantum yield was in dichloromethane relative to 2-aminopyridine in 0.1 N H_2SO_4.