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Synthesis of Dendronised and Dialkyl Fluorene Based Hybrid Polymer under Microwave Irradiation

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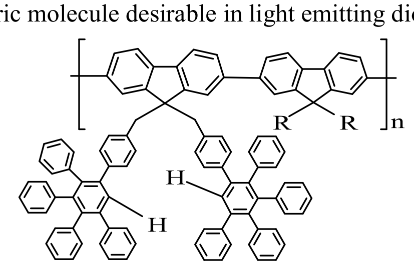
Abstract: *We report a rapid synthetic strategy to afford of new dendronised and dialkyl fluorene based hybrid polymer by employing Microwave radiations. This polymer was synthesized by the reaction of 2,7-dibromo-9,9-di(4-(2,3,4,5-tetraphenylphenyl)benzyl) fluorene with 2,7-dibromo-9,9-dipentyl fluorene under microwave irradiation using nickel catalyst. The synthesized dendronised and dialkyl fluorene based hybrid polymer was fully characterized by spectroscopic techniques. We believe that, this dendronised and dialkyl fluorene based hybrid polymer can be emerge as a promising material for blue-light-emitting diodes.*

Keywords: Fluorene; Polyphenylene; Dendrimers; Microwave; Polymerization

I. Introduction

In the present scenario of chemical synthesis, the term "green chemistry" is well acknowledged in scientific community 1-3. Green chemistry based synthetic methods offer energy savings and waste reduction 4. Chemical synthesis by using Microwaves has become very useful and efficient method 5. Microwave heating efficiently reduces reaction times and increases reaction yields, while simultaneously reducing the amount of unwanted by-products 6,7. Our literature survey in this context showed that, the synthesis of conjugated polymers under microwave irradiation is advantageous as compared to conventional heating 8-10. In the present scenario, synthesis of polymeric materials has increased significantly owing to their usefulness in a wide variety of fields 11-17. In the diverse range of polymeric materials, "dendronized polymers" are important because of their sole structural features and applications in the ample fields 18-20. Likewise, fluorine based polymeric materials have become popular in optoelectronics because of their excellent thermal and photo-physical properties 21-23. Amongst them, alkyl substituted polyfluorenes (PFs) are becoming very popular blue-emitting material 24,25. The properties of PFs can be molded by bringing donor or acceptor group of phenyl rings of fluorene molecule 26-29. The 2,7 positions of phenyl rings of fluorene unit provide opportunities for synthesis of conjugated polymer chain using electrophilic substitution reactions 30. Due to significant importance of alkyl substituted fluorenes and polyphenylene dendron substituted fluorenes in polymer based light emitting diodes 31, we envision the new molecular framework containing both of these units in single nucleus (Figure 1). We believed that, the polymeric framework which assimilates fluorene unit as well as a polyphenylene Dendron unit might integrate properties of both, and the synergism of these frameworks in a single nucleus may result in the formation of some worthwhile polymeric molecule desirable in light emitting diodes.



R=Alkyl

Figure 1: Envisioned polymeric framework

In this context, we planned the synthesis of new dendronised and dialkyl fluorene based hybrid polymer. We herein report microwave assisted rapid and efficient synthesis of new dendronised and dialkyl fluorene based hybrid polymer.

II. Experimental

2.1 Materials

All required chemical materials were ordered from SD Fine Chemicals, Mumbai. Solvents used for work-up and purification process were freshly distilled. Bruker AMX-300 spectrometer was used for recording NMR spectrums and CDCl3 and tetramethyl silane (TMS) were employed as a solvent and internal standard respectively. Perkin–Elmer, Frontier-91579 series FT-IR/FIR spectrometer was used to record FT-IR spectrums. UV-Visible spectra were recorded by Shimadzu UV-2450 UV/Visible spectrometer of wavelength range 200-800 nm. MAS-II Microwave Synthesis Workstation was employed to synthesize polymers.

Synthesis of Characterization of new Dendronised and Dialkyl Fluorene based Hybrid Polymer

General Procedure for preparation of Dendronised and Dialkyl Fluorene based Hybrid Polymer:

In the reaction vessel bearing 20 ml of DMF : toluene (1:4) system, the 0.5 g of bis(1,5- cyclooctadiene)nickel (0), 0.35 g of 2,2'-bipyridine and 0.25 ml cyclooctadiene were added. The reaction mixture was stirred under an inert atmosphere of nitrogen. To this solution, 0.250 g of 2,7-dibromo-9,9-di(4-(2,3,4,5-tetraphenylphenyl)benzyl) fluorene and 0.250 g 2,7-dibromo-9,9-dipentyl fluorene was added. This reaction mixture in the vessel was sealed and kept in a microwave reactor. The reaction vessel was maintained at 130°C with 300 W powers for 20 min using microwave radiation. After 20 min of heating, the end capping the polymerization process was done by adding 5 ml of bromobenzene to the reaction mixture. This mixture was further heated for 5 min under similar condition. The reaction mixture was cooled to room temperature. To this cooled reaction mixture, 20 ml dichloromethane was added for dilution. The diluted reaction mixture was washed several times with water. The obtained organic layer was collected, dried over magnesium sulfate and concentrated to nearly dryness. In this extract, 20 ml of acidified methanol solution (0.5 M HCl) was added to precipitate polymer.

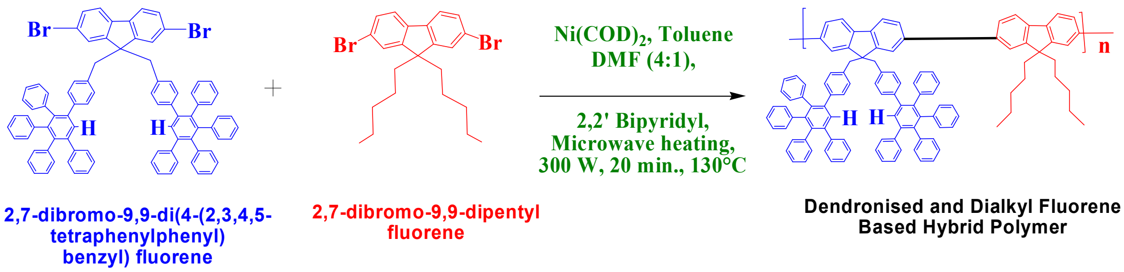
Characterization Data of Dendronised and Dialkyl Fluorene based Hybrid Polymer

Gray solid. Yield 91.10 %, ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.72-1.09 (m, 110 H of alkyl group), 2.02 (s, 20 H of benzyl group), 6.85-7.64 (m, 320 H of Ar ring) ppm. IR (KBr): ν_{max} = 3032, 2926, 1493, 1599, 1441 cm^{-1}.

III. Results and Discussions

3.1 Synthesis of Monomer and Polymer

The monomer 2,7-dibromo-9,9-di (4-(2,3,4,5-tetraphenylphenyl)benzyl) fluorine was synthesized as per the methods reported in our previous work [32]. The synthesis of monomer 2,7-dibromo-9,9-dipentyl fluorene was achieved by method reported by *Iyer et al* [33] with slight customized modifications. Then after, the synthesis of desired new dendronised and dialkyl fluorene based hybrid polymer was accomplished by the polymerization of monomer 2,7-dibromo-9,9-di(4-(2,3,4,5-tetraphenylphenyl)benzyl) fluorine with 2,7-dibromo-9,9-dipentyl fluorene. We mixed and stirred the 0.5 g of bis(1,5- cyclooctadiene)nickel (0), 0.35 g 2,2'-bipyridine and 0.25 ml cyclooctadiene in 20 ml of DMF : toluene (1:4) system under nitrogen atmosphere. To this stirred reaction mixture, 0.250 g of 2,7-dibromo-9,9-di(4-(2,3,4,5-tetraphenylphenyl)-benzyl) fluorene and 0.250 g of 2,7-Dibromo-9,9-dipentylfluorene was added. This reaction mixture in the vessel was sealed and kept in a microwave reactor. The reaction vessel was heated at 130°C using 300 W power for 20 min under the microwave reactor. After 20 min of heating, the end capping the polymerization process was done by adding 5 ml of bromobenzene to the reaction mixture. The reaction mixture was then further heated for another 5 min at same reaction condition and then cooled to room temperature. To this cooled reaction mixture, 20 ml dichloromethane was added for dilution. The diluted reaction mixture was washed several times with water. The collected organic layer was dried over magnesium sulfate and concentrated to nearly dryness. In this extract, 20 ml of acidified methanol solution (0.5 M HCl) was added. The polymer gets precipitated to afford 91.10 % yield. The obtained product was extensively characterized by different spectroscopic techniques which confirmed the formation of desired dendronised and dialkyl fluorene based hybrid polymer. In the persistence of our research [34-36], herein we have demonstrated the synthesis of new dendronised and dialkyl fluorene based hybrid polymer in the presence of bis(1,5- cyclooctadiene) nickel (0), 2,2'-bipyridyl, cyclooctadiene, in toluene : DMF (4:1) system under microwave irradiation at 130°C using 300 W power for 20 min in the presence of N_2 atmosphere (**Scheme 1**).



Scheme 1: Synthesis of new dendronised and dialkyl fluorene based hybrid polymer by employing Microwave radiations

IV. Conclusion

In conclusions, we have demonstrated microwave assisted an efficient synthesis of new dendronised and dialkyl fluorene based hybrid polymer by polymerization of polyphenylene substituted dendronised monomers containing fluorene unit namely 2,7-dibromo-9,9-di(4-(2,3,4,5-tetraphenylphenyl)-benzyl) fluorene with 2,7-Dibromo-9,9-dipentylfluorene under microwave irradiation using nickel catalyst. The synthesized new dendronised and dialkyl fluorene based hybrid polymer was extensively characterized by different spectroscopic techniques which confirmed the formation of desired dendronised and dialkyl fluorene based hybrid polymer. The synthesized desired dendronised and dialkyl fluorene based hybrid polymer found non-hygroscopic and stable gray solids soluble in common organic solvents like $CHCl_3$, DMSO, THF. We proposed that this dendronised and dialkyl fluorene based hybrid polymer may emerge as a useful materials for OLED's.

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