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摘要:

摘要: 以3,4,9,10-哌啶四羧酸酐为原料, 以L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally为侧链, 通过逐步胺解反应, 合成了不对称的聚肽类PDI。研究了反应条件对产率的影响, 确定了最佳反应条件: 哌啶四羧酸酐与环己胺的摩尔比为1:6, 溶剂体积比为乙醇:水=4:1, 反应温度为70℃, 反应时间为6 h, 得到中间产物N-环己基-3,4,9,10-哌啶四羧酸-3,4-酐-9,10-酰亚胺。在DMAP催化下, 该中间产物与L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally在120℃下反应4 h, 得到目标产物, 总产率高于32.6%。产物结构经ESI-MS和¹H-NMR表征。

关键词: 聚肽类PDI; 逐步胺解反应; 不对称PDI; 3,4,9,10-哌啶四羧酸酐

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Synthesis of polypeptides with asymmetric perylene diimide side chains

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Abstract: Perylenetetracarboxylic diimides (PDI) and their derivatives have been paid more attention due to their special photophysical and electrochemical properties. The modification on molecular structure of PDI aimed at changing the photophysical properties is one of an important means to obtain functional materials of PDI. An asymmetric PDI containing polypeptide chain at one imide nitrogen is synthesized by stepwise aminolysis reaction of 3,4,9,10-perylenetetracarboxylic dianhydride. The influence of reactions on yield is then inquired. The optimal reaction condition are determined as follows: molar ratio of PDI to cyclohexylamine, 1 : 6; the solvent volume ratio of ethanol to water, 4 : 1; reaction temprature and time, 70 °C and 6 h, the intermediate N-cyclohexyl-3,4,9,10-perylenetetracarboxylic-3,4-anhydride-9,10-imide. In the presence of the catalyst DMAP, this intermediate undergoing aminolysis reaction with L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally affords polypeptides with asymmetric PDI in imidazole for 4 h at 120 °C, and the tatal yield is above 32.6%. The product structure is characterized by ESI-MS

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and $^1\text{H-NMR}$. The process is simple and mild conditions, which provides a convenient synthetic route for the preparation of asymmetric PDI compounds.

Keywords: organic synthesis chemistry; perylene anhydride; perylene diimide; asymmetric; chain tetrapeptide; synthesis

π - π stacking interaction, which is a key factor in the self-assembly of perylene diimide (PDI) derivatives. The introduction of functional groups on the perylene core can significantly affect its photophysical properties and self-assembly behavior. For example, the introduction of hydrophilic groups can improve the water solubility of PDI, while the introduction of hydrophobic groups can promote its aggregation in aqueous solution. The synthesis of asymmetric PDI compounds is a challenging task, but it is essential for the development of new materials and applications. This paper reports a simple and mild synthetic route for the preparation of asymmetric PDI compounds. The reaction involves the condensation of perylene tetracarboxylic dianhydride with a diamine in the presence of a catalyst and solvent. The resulting PDI derivatives exhibit unique photophysical properties and self-assembly behavior, which are discussed in detail in the text.

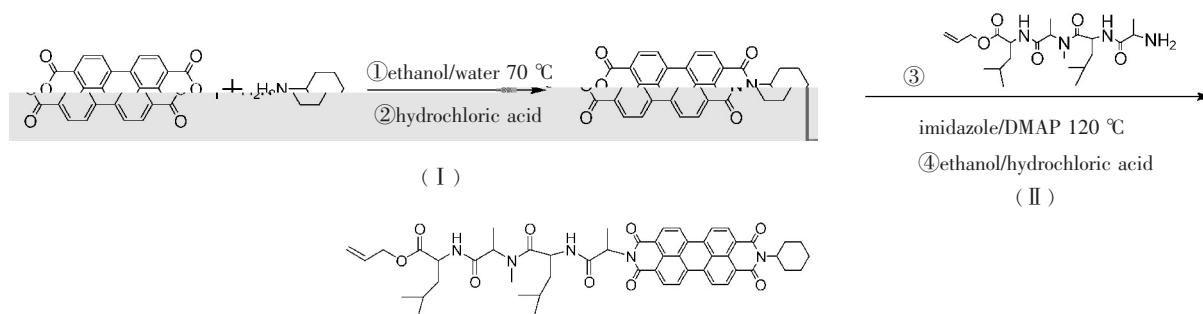
1 实验部分

1.1 主要仪器与试剂

500 MHz Bruker; 500-MS; Varian; DMAP, 3,4,9,10-perylene tetracarboxylic dianhydride; L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Allyl [15].

1.2 实验过程

N-cyclohexyl-N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Allyl)-3,4,9,10-perylene tetracarboxylic diacyl amine (I) was synthesized according to the following procedure:



1 N-cyclohexyl-N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Allyl)-3,4,9,10-

Fig.1 Synthesis route of N-cyclohexyl-N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Allyl)-3,4,9,10-perylene tetracarboxylic diacyl amine

1.2.1 N-cyclohexyl-N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Allyl)-3,4,9,10-perylene tetracarboxylic diacyl amine (I) was synthesized according to the following procedure: 1 g (2.5 mmol) perylene tetracarboxylic dianhydride, 2.5 mL (20 mmol) N-cyclohexyl-1,4-diaminobutane, 500 mL ethanol, 20 mL imidazole, 80 mL DMAP, 70 °C 6 h. The resulting product was purified by column chromatography (0.045 μm silica gel, (30 mL \times 2), 30 mL \times 2).

mL×2) , N- -3,4,9,10- -3,4- -9,10- ,

1.2.2 N- -N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally)-3,4,9,10-
 N- -3,4,9,10- -3,4- -9,10- L-Ala-D-Leu-(N-Me)-Ala-D-Leu-
 Ally 2.7 g(5 mmol) 500 mL , 12 g(176 mmol) DMAP 0.000 5 g
 (0.004 mmol), 120 °C 5 h。 , 50 mL ,125 mL
 (2 mol/L), 。 0.045 μm , (30 mL×2)、
 (30 mL×2) , 。 (V() V()=70 1),
 N- -N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally)-3,4,9,10- , 32.6%。
 ESI-MS ¹H-NHR 。 ESI-MS (m/z):918.4[M+Na]⁺; ¹H-NHR(500
 MHz,CDCl₃-d),δ:8.91(d,4H),8.74(d,4H),5.78(m,1H),5.24(m,2H),4.59(m,4H),4.12(s,2H),3.66
 (m,1H),2.98(s,3H),1.72~1.79(m,6H),1.25~1.42(m,16H),0.95(s,12H)。

2 结果与讨论

3,4,9,10- , , :1)
 。 [16-17];2) /
 , [12];3) [18]。
 、 、 。
 , 3,4,9,10- ,
 。 ,
 , π-π
 , ,
 , V() V()=1 100 , ,
 。 、 、 、 。

2.1 溶剂的影响

1 。
 , V() : V() =4 : 1
 N- -3,4,9,10- -3,4- -9,10-
 , 。 /
 ,
 。 / , N-
 -3,4,9,10- -3,4- -9, 10-
 , ,
 ,

1

Tab.1 Effect of solvents

	/%
1	0
2	0
3 V() : V()=4 : 1	32.6
4	0

: n() : n()=1 : 6; (I) 70 °C ,
 (II) 120 °C; DMAP。

2.2 物质的量比的影响

2 ,
 ,
 n() n() = 1 6 ,
 32.6%;
 。

2

Tab.2 Effect of different ratio of reactants

n()	n()	/%
1	1 10	27.7
2	1 6	32.6
3	1 1	13.3

: V() V()=4 1; (I) 70 °C ,
 (II) 120 °C; DMAP。

2.3 催化剂的影响

DMAP, DMAP, DMAP, [19-22], N-4-

3
Tab.3 Effect of catalyst

	DMAP /mmol	/%
1	0	5.3
2	0.002	26.7
3	0.004	32.6
4	0.010	32.6

: 5 mmol; n() n()=1 6; V() V()=4 1; (I) 70 °C, (II) 120 °C。

2.4 反应温度的影响

4。
4

Tab.4 Effect of reaction temperature

	/°C		/%
	(I)	(II)	
1	70	110	25.8
2	70	120	32.6
3	70	130	23.6
4	60	120	19.3
5	80	120	27.9

: n() n()=1 6; V() V()=4 1; DMAP。

1,2,3, (I), (II), 120 °C, 2,4,5, (II), (I), 70 °C,

3 结 语

3,4,9,10- / (V() V()=4 1) 70 °C 6 h, N- -3,4,9,10- -3,4- -9,10- ; L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally, DMAP, 120 °C 4 h, N- -N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally)-3, 4,9,10- 32.6%。 DMAP,

参考文献/References:

[1] GUAN Y, YU S H, ANTONIETTI M, et al. Synthesis of supramolecular polymers by ionic self-assembly of oppositely charged dyes[J]. European Journal of Chemistry, 2005, 11(4): 1305-1311.
[2] LI X Y, SINKS L E, RYBTCHINSKI B, et al. Ultrafast aggregate-to-aggregate energy transfer within self-assembled light-harvesting

- columns of zinc phthalocyanine tetrakis(perylene₂diimide)[J]. Journal of America Chemistry Society, 2004, 126(35): 10810-10811.
- [3] LU W, GAO J P, WANG Z Y. Electrochemical characterization, electrochromism, and voltage-dependent fluorescence of novel perylene-containing polyimides[J]. Macromolecules, 1999, 32(32): 8880-8885.
- [4] . [D]. : ,2007.
FENG Yiyu. Preparation and Characterization of Photo-responsive Organic Conjugates and Carbon Nanotubes [D]. Tianjin: Tianjin University, 2007.
- [5] WURTHNER F, SAHAMOLLER C R, FIMMEL B, et al. Perylene bisimide dye assemblies as archetype functional supramolecular materials[J]. Chemical Reviews, 2016, 116(3): 962-1002.
- [6] KUMAR J, NAKASHIMA T, TSUMATORI H, et al. Circularly polarized luminescence in supramolecular assemblies of chiral bichromophoric perylene bisimides[J]. European Journal of Chemistry, 2013, 19(14): 14090-14097.
- [7] KUMAR J, NAKASHIMA T, KAWAI T, et al. Circularly polarized luminescence in chiral molecules and supramolecular assemblies[J]. Journal Letters, 2015, 6(17): 3445-3452.
- [8] KUMAR J, TSYMATORI H, YUASA J, et al. Self-discriminating termination of chiral supramolecular polymerization: Tuning the length of nanofibers[J]. Angewandte Chemie International Edition, 2015, 54(20): 5943-5947.
- [9] , , , . [J]. ,2012,26(17):92-102.
XU Yewei, ZHU Fanghua, ZHANG Hailian, et al. Progress in functional materials containing perylene[J]. Materies Review, 2012, 26(17): 92-102.
- [10] ZHAN X W, TAN Z A, DOMERCQ B, et al. A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells[J]. Journal of America Chemistry Society, 2007, 129(33): 7246-7247.
- [11] YAO D J, WANG Z Y, SUNDARARAJAN P R. Time dependent crystal-smectic transformation in perylene-containing polyimides[J]. Polymer, 2005, 46(12): 4390-4396.
- [12] STRUIJK C W, SIEVAL A B, DAKHORST J E J, et al. Liquid crystalline perylene diimides: Architecture and charge carrier mobilities [J]. Journal of America Chemistry Society, 2000, 122(45): 11057-11066.
- [13] KOLHE N B, ASHA S K, . a