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(, 050018)

摘 要: 。

, 。 3,4,9,10- ,
L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally ,
。 、 、 , 。
: n( ):n( )=1:6、 / (V( ):V( )=4:1)、 70 ℃ 6 h, N- -3,4,9,10- -3,4- -9,10- ; L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally , 4- (DMAP) , 120 ℃ 4 h, N- -N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally)-3,4,9,10- , 32.6%; ESI-MS ^{1}H-NHR 。 , ,
。

关键词: ; ; ; ; ;

中图分类号:O62 **文献标志码:**A

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 ℃ 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 ℃, and the tatal yield is above 32.6%. The product structure is characterized by ESI-MS

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and ^{1}H-NHR. 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

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π-π , 、 ,

, 。 ,

, 。 , ,

[1-2]。 [3-8]、 、 、 、

[9-10]、 (liquid crystal)[11-12] 。

, π-π ,

(、 、)。 π-π

, , , [13]。

, 。

[14], 。

, 。

, 、 、 ,

, , 。

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, 。

1 实验部分

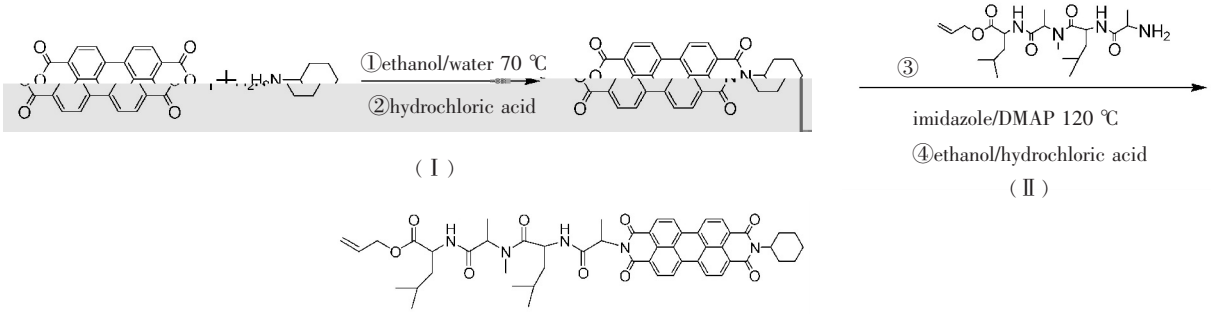
1.1 主要仪器与试剂

500 MHz , Bruker ;500-MS - , Varian 。

、 , ;DMAP、 、3,4,9,10- , ;L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally , [15] 。

1.2 实验过程

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



(Ⅰ) (Ⅱ)

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

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

1.2.1 N- -3,4,9,10- -3,4- -9,10-

3,4,9,10- 1 g(2.5 mmol) 2.5 mL(20 mmol), 500 mL , 20 mL 80 mL , 70 ℃ 6 h。 , 250 mL (2 mol/L), 。 0.045 μm , (30 mL×2)、 (30

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 ℃ 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 ^{1}H-NHR 。ESI-MS (m/z):918.4[M+Na]$^+$;^{1}H-NHR(500 MHz,$CDCl_3$-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 。 1
, V( ):V( )=4:1 Tab.1 Effect of solvents

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

N- -3,4,9,10- -3,4- -9,10- :n( ):n( )=1:6; (Ⅰ) 70 ℃,
, 。 / (Ⅱ) 120 ℃; DMAP。
,
。 / , N- 2
-3,4,9,10- -3,4- -9, 10- Tab.2 Effect of different ratio of reactants
, ,
, , n( ) n( )
, n( ) n( )=1 6 , /%
, 32.6%; 1 1 10 27.7
。 , 2 1 6 32.6
3 1 1 13.3

2.2 物质的量比的影响

2 , : V( ) V( )=4 1; (Ⅰ) 70 ℃,
, , (Ⅱ) 120 ℃; DMAP。

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2.3 催化剂的影响

，　　，

DMAP　　，　　3。　　3

，　　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 ℃，　(Ⅱ)　　120 ℃。

2.4 反应温度的影响

4。

4

Tab.4 Effect of reaction temperature

	/℃		/%
	(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 ℃　　。　　，　　；　　，

，　　。　2,4,5　　，　(Ⅱ)　、　(Ⅰ)　，

，　　70 ℃　，　　。　　，　　，

，　　，　　。

3 结　语

3,4,9,10-　　，　　/　　(V(　　)　V(　　)=4　1)

70 ℃　6 h，　、　N-　-3,4,9,10-　-3,4-　-9,10-

；　L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally　　，DMAP　、120 ℃

4 h，　、　、　，　N-　-N'-(L-Ala-D-Leu-(N-Me)-Ala-D-Leu-Ally)-3,

4,9,10-　　，　32.6%。

，　　，　　，

。　DMAP　　，　　，

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