[Article]

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POPOP 诱导环糊精形成纳米管的研究

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摘要 689:; <=>?@A<>A<BCDEFG@<HIJKLMN02,2!"p"PQR"S(5"QR嚥T) (POPOP)()1UVW(CD)XYZ[6.\]^_, POPOP() `abcde1 β "CDfg1#2Xhi ,`a bcjekImnopq β "CDfgrst\u.vewx, POPOP()ykIpq γ "CDfgrst\u.z (| β "CD, POPOP()` γ "CD}~· XA<wl!, "#\$_%X&'()y*+OW, \u, -xc. XOh!./O1| POPOP()gzm2 γ "CD 34fg05R6i X78.pHF9b:5-.mno^_, POPOP pq β "CDfgXrst`pHO| 12F9bj| 331 KXU; <"=?>?`.

关键词: rst, UVW, A<BCDE, G@<HI 中图分类号: O641.3

The ormation of yclodextrin Nanotube nduced by POPOP olecule

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bstract The interaction between 2,2!"p"phenylenebis (5"phenyloxazol) (POPOP) and cyclodextrins (CDs) was investigated using UV"Vis absorption, steady"state fluorescence, and dynamic light scattering (DLS). The results indicated that POPOP could form the 1#2 (guest:host) inclusion complex with β "CD at lower concentrations, which could further form the extended nanotube at higher concentrations. POPOP could also induce the formation of the nanotube of γ "CD. The fluorescence emission of POPOP in aqueous solution of γ "CD showed obvious red shift accompanied by the disappearance of fine structure compared with that in aqueous solution of β "CD, which could be attributed to the formation of the excimer of POPOP in the larger cavity of γ "CD. It was found that at pH greater than 12, the hydrogen bond between the neighboring CDs was destroyed, which led to the collapse of the nanotubular structure. The results also showed that the nanotube structure was not stable at temperatures above 331 K.

eywords: Nanotube, Cyclodextrin, Fluorescence anisotropy, Dynamic light scattering

@ 1994 A McGown BCD^[1]\$EOFGH 1, 6"I QRJKL(DPH)() = 1 β "CD F γ "CD $\hat{}$ ~• MN() O[6P@DQfgrsRbX t STUVI W, MNXz/n@DQxYZ[O a\X] ^. Pistolis J ^[2]6?@A<_A<BCD EKLz DPH () 1UVW $\hat{}$ OXYZ[6m aOb2XMN.MN\]^_ DMF/}ci ~ d , DPH () ykl pq β "CD F γ "CD fgr st. MN DPH () Xe[fNO2"DPH F N (CH₃)2"DPH 1UVW[6e, gwx" = fgr st^[3]hvi , j γ "CD XkRI 6mnRopq, r st y" = fg^[2]. Pistolis J^[4]r MNO DPH () Xst v7 , 1, 3"FGHI QRuI L(DPB)F 1,3,5,7"FGHI QRvwL(DPO)1UVWXYZ

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^{+, @}x* #Ry(90206020, 29901001)z { | }

[6,\]^_rstXfg1()XR \$,c HI 90\$. **9b** 25%. н R X DPB () =1UVWfghi ,(c <,21 <X b5 k= , k Х R X DPO ()g pqUVWfgrs 0 &5'.**89:;<=** 6 U"3010 t. Agbaria J ^[57]XMN ^_, wt 噤T () Xe (Hitachi) **89"k (<<b** , < [, f 2,5"] QR"1,3,4"] 账T(PPD)≥,5"] QR ?@A<wl_A<BCDEX 6 F"4500 「地子(PPO)>2"QR"5"(4"IQR)"1,3,4"I 感T(PBD)F (Hitachi)A<(<<b ,5wFwIX 2,5"(4,4!"I QR)"1,3,4"I 账T(BBOD), yki pq 10 nm. \$ 9b: 5-. . . 6 U} 9. γ"CDfg Xrst\uh`/ rstXf H9b (Checktemp, Hanna, Italy. 6nt gN3 , \mathbb{K} T () I Ogz m2 γ ^{*}CD 3 W b & 0.1%) 2i XA<<= |\$5R6i . 9b. 4 **x**./ A<() Xn 实验方法 н () q = POPOP ~ . \$ ()X< wg(~ • ab 9, y\$MN^_, n $10^{-4} \text{ mol } L^{-1} \mathbf{X}$ () ykl) . • . 6 mi Ο pqUVWfgrstX\u[®]. Х • (POPOP • V Ni n AW, BCDy P X1')Fn>V XUVW~•| / = pqUVWfgrstX\$ () `0 -. К }> .\$ pH:5X-.,~•XpH wxO10t/iX ()^[9'14]/ n" XR **6** 0.1 mol L⁻¹ **X** F \]^_, ()?`<UVWrstXfgk @ < H I Xi **6** 0.2 μm (Membrana, micro PES) X =Ontc XxY. N . 1 2,2!"p"PQR"S(5"QR账T)(POPOP)()()() XO)_3 Х $\mathbf{k} = \mathbf{W} \mathbf{X}$ 1)**E n** XA< Х uН VF 6 ()> Y9b > JMN ^[15"21]. **A**< **689:** ; <=> 结果和讨论 ?@A<<=FG@<HI J - . POPOP 分子在不同溶剂中的紫外吸收光谱 MNwx. POPOP () $y = pq \beta^{"}CD F \gamma^{"}CD f gr st$. POPOP () ` } > > $\mathbf{F} \alpha$ "CD, β "CD, γ"CD **}~• X89:**; <= 2 .1 k 实验部分 , Yz | } ~• **O:**; **! X!**, POPOP (**\$&'**, ` α"CD **} ~•** 试 剂)`m F **'**, (` β "CD **F** γ "CD **} ~• \$_%** α "CD(Acros, \geq 98%), γ "CD(Aldrich, 99%) \$ POPOP(Acros, Laser Grade) 6. β"CD(&' S 8.0 U"# d (} \ s)**6K** 6.4 a 6.-. **6X** d (· mol⁻¹. `/9<ma. _, - . 4.8 仪 器 G@<HI<= 6 ALV/DLS/SLS" 0_1.6 5022F <) Y (< .5< X 632.8 nm, 0.0 + 500: :: 300:0:350:0 400 :: 450 : E 550 💠 600 λ^2 / nm 冬 POPOP 分子的紫外吸收光谱 UV-Vis spectra of POPOP ig 冬 POPOP 的分子结构式 $c(POPOP)=2.5(10^{-6} \text{ mol } L^{-1}, c(CD)=15 \text{ mmol } L^{-1};$ olecular structure of POPOP) water,) ethanol, """) n"heptane, ig - \bigcirc -) α "CD, - \blacktriangle -) γ "CD, - \blacklozenge -) β "CD POPOP%2,2!"p"phenylenebis(5"phenyloxazol)

X

Х

2.5(

POPOP

~ •

2

. **G**

2 nm.

L

i

X&'`qs ~•, r `420 600 nm \$_%XHI xY -POPOP/a"CD } ~• ~•, (POPOP'β"CD F POPOP'γ"CD } ~• xn>3bX qXX! ?`n> POPOP-β- 溶液中 : 包合物的形成 POPOP () `"vab β"CD } ~• XA <wl <= 3a kl ,POPOP () ` dab(4.0(10⁻⁸ mol L⁻¹)eXA < b β"CD ab! (!O(eV7-"F \$@).ve, POPOP () `β"CD } ~• XA < { } 1 ` }





图 POPOP 分子的稳态荧光各向异性值 r

ig Steady-state fluorescence anisotropy *r* of POPOP

) ○)) β- CD;) ●)) γ- CD; c(POPOP)=2.5(10⁻⁶ mol·L⁻¹

F γ "CD **X Oab** 0.015 mol L⁻¹**e**, POPOP **X** r (j: 0.28 F 0.29. (z | POPOP () ~ **X** r # 0.06. POPOP () β "CD F γ "CD } ~· A<BCDE X! O, ^_ e POPOP () X; G< O OX= ^[23],/nxYk6r stXfgW > `rst hi|UVW34 X POPOP() X?; < O OX = ,@(**^x cj X**r . POPOP ~ γ"CD **} ~• ΧΑ** <wl!, Yz | β"CD } ~• "#\$_%X& ',()^A()W,\uX !yB+0,-xn .!./01| γ "CD 34cO, POPOP () gz **m2** γ["]CD **34fg5R6i X78**. , **C x** POPOP() = $pq\beta^{"}CD F \gamma^{"}CD I f gr st$ \u, D POPOP () `/s rst X \$ "V. X, POPOP () R O1tX E **h(`qX**, OgzX E `89:;FA<wl<= X!fF! O"ni X. Teale^[24]EF. N GHXHI <zA< Х BCDE ntJ KH f , I $(r' - r_{obs})/r! = (3-3T)/(3+7T)$ (1)H r! - LXA < BCDE , r_{dbs} O XA< BCDE , TOMI <X b12I <X b **{**. q, Lentz J^[25]N O+J XOP KH. V7 XQ6E I Ont R EXJ **KH%** $(r!-r_{obs})/r!=K\times A$ (2)

HK (S, A: <b.

1|cOR UVWrstXfg POPOP(2.5(10⁻⁶ mol L⁻¹)" β "CD(0.015 mol L⁻¹) POPOP(2.5(10⁻⁶ mol L⁻¹)" γ "CD(0.015 mol L⁻¹)**X**C , ` 6 POPOP () XA< i ~• - x Χ BCDE (F. TC \$UVz+V7 XA<BCDE maj . W I **On7** "vab^β" XJ KH(1)F(2),CD } ~• POPOP(2.5(10⁻⁶ mol L⁻¹) () X: < XYZ, 1: <b Ь (6). **I : <b** Г **KH**(1)**JH\]X** (3- 3T)/(3+7T)**II** $\mathbf{YZ}(\mathbf{+} \mathbf{y}_{O}(\mathbf{r}! - \mathbf{r}_{ds})/\mathbf{r}!\mathbf{XO}$, ! 3` GHXa-A<BCDE b Xc(1 GHXa- 1)[bXO f 1 X)i\]^_sX-(eX E 6. 7, EY b 0.999. X/n\]R fi Teale MNDX! . ^[24]. 1HI <GHXBCDE Xa-**OXd 1 : <b-{\$ 7 1J** KH(1)kl $[(r! - r_{obs})/r!, (r_{obs} k)$

11-. , **1 kl** Г a-XA<BC **DE** r!. 7 , j β "CD abc e, r! 1 **b** β "CD **abcOe**, r!**1** r_{drs} **d** r_{obs} d O" N 4'. , **k' Z** | POPOP (2.5($10^{-6} \text{ mol } L^{-1})"\beta"CD(0.015 \text{ mol } L^{-1})Xci \sim 0, j r$ stfgqGHX z POPOP() A<B **kig** . (z | PBD(1.0(10⁻⁵ mol CDE X



图 不同浓度的 β- 水溶液中 POPOP 分子荧光各向异 性真实值与测量值之间的偏^之 r' r_{obs} r' 与₋-颠光 度 A 的关系

```
ig ependence of r' r_{obs} r' of POPOP vs
absorbance in aqueous solutions of \beta- at
various concentrations
from 1 to 13, c(\beta"CD)=0, 0.6, 1.2, 1.8, 2.4, 3.0, 4.5, 6.0, 7.5,
9.0, 10.5, 12.0, 13.5 mmol L<sup>-1</sup>
```

(3)



- 图 不同浓度β-水溶液中 POPOP分子 × mol· 校¹ [●] 的 -○- 和实 ^④测量的 -●- 荧光各向异
 性值以及单根 POPOP-β- 纳米管中所含环糊精单
 元数目的估算 -■-
- ig orrected $-\bigcirc$ and observed $-\bullet$ fluorescence anisotropy of POPOP × mol· in aqueous solutions of β - at various concentrations and the estimation of unit in a single POPOP- β - nanotube $-\blacksquare$ -

L⁻¹)"³"CD (0.01 mol L⁻¹)Xci ~•, 1 | V7 \$ UVWrstI TUVXfg ~• (_%, J A<BCDEewxd O 24', / hi <X zA<BCDE X O'' =g X^[14].

?@A<BCDE X > jOn
k[rst UVW1I }XKL.W Perrin"
Weber KH^[23]

 $r_0/r=1+\tau RT/\eta V$

 r_0 () X OA<BCDE, M | 273 Ke mn >. z| POPOP() (o, r_0 0.33. τ ^ A<pq, η ^ rsXt

b. τ **F** η **ku>''%**^[13], **vwA<BCDE r X%''_1rstXR Y**, **W H**(4)^[2]**k I k[** POPOP' β ''CD **rstXR**

 $[\mathbf{r}_{2}(\mathbf{r}_{0} - \mathbf{r}_{1})]/[\mathbf{r}_{1}(\mathbf{r}_{0} - \mathbf{r}_{2})] = \mathbf{V}_{2}/\mathbf{V}_{1}$ (4)

 $r_1 \mbox{ F } r_2 \mbox{ OS } V7 \mbox{ POPOP () XA < BC } DE \ , V_1 \mbox{ F } V_2 \ / \mbox{ S } V7 \ \mbox{ POPOP () X$ } $: V \ . \label{eq:r1}$

k [POPOP" β "CD rst UVW11 } (n_{cD})**e**, **x** ("vab β "CD ~• POPOP () **XA<BCDE** (r₂). **G2** 1#2 (POPOP# β "CD) **XA<BCDE** (c(POPOP)=4.0(10⁻⁸ mol L⁻¹, c(β " CD)=0.007 mol L⁻¹, r₁=0.13), vw 2((V₂/V₁) **X** _

Yj | rst UVW1IX }. | O,W J 1Wrst β"CD **1Ι Χ** qXr!,k[. POPOP' β "CD rst 7 3.13 . β" CD 1| X } Ο 19. 动态光散射的测量 Gonzalez"Gaitano MND²⁶E6G@<HI y $z MNO \alpha$ "CD \gg "CD F γ "CD \rightarrow } ~• BD(X {(|,\]^_UVW`}~• }0 (I 1VXfH?`, vey\$ **XTUVI ?** BCD y`/K~•On 2[, X\. 1 献[26]\$E\]R n f/K UVW[~] }~• l?`s S@, n 流VP#半{` 0.6 0.8 nm 左**丶ㄨ1Ⅴ**, 流**VP#**半{ ` 60 100 nm 左丶X团簇TUV^[13]. 8 OYvab $(0.015 \text{ mol } L^{-1})$ XK UVW }~• **2n>** X POPOP () $(2.5(10^{-6} \text{ mol}))$ L⁻¹)**qXG@<HI** =, Y5X **| ^** 1. @ 8**F^**1 **wx**, **z** | α "CD } ~• , 2 " POPOP() z BD(XR O _(| . 换o`, POPOP () 1 α"CD ` Ok= fgn 01Xhi ,(/ hi X {0 跟 α"CD **1 VX** "O. sXXG@<HI = .x(z| **\$** POPOP () $X \beta$ "CD $\mathbf{F} \gamma^{"} CD \} \sim \bullet$. O **UVWX1VFTU** VX! | 9, r nt 流VP#半{ 15 nm 左ヽX !./1 W6G@<HI yzMN N, N!"diphenyl"benzidine () 1 CD [6e



- 图 加入 POPOP 分子的水溶液^线 -μm 滤膜_过滤^厂的 动态光散射图谱
- ig S results of POPOP in the aqueous solutions filtered with the $-\mu$ m filter The inset is the enlargement of R_h ranging from 5 to 25 nm; c(POPOP)=2.5(10⁻⁶ mol L⁻¹, c(CD)=0.015 mol L⁻¹;) $\alpha^{"}CD$, ---) $\beta^{"}CD$,) $\gamma^{"}CD$

动态光散射测量中 环糊精及环糊精中加入 POPOP 分子的溶液中各组分的 耒 平均流体力学半径 R_h 、相对散射光强 I和质量分数 w的数据

Table 1 Mean hydrodynamic radius (R_b), correlative intensity (I), and mass fraction (w) contributions of

various components in the aqueous solutions of CDs and POPOP"CDs

Sample	R _{h1} / nm	I ₁ (%)	w1 (%)	R _{h2} / nm	I ₂ (%)	w ₂ (%)	R _{h3} / nm	I ₃ (%)	w ₃ (%)
α "CD [*]	0.6&0.1	6.68	99.9989	-	-	-	64.4&0.5	93.32	0.0011
POPOP"α"CD	0.7&0.2	6.56	99.9989	-	-	-	114.2&0.5	93.44	0.0011
β "CD *	0.8&0.1	14.02	99.9998	-	-	-	114.7&0.4	85.98	0.0002
POPOP" β "CD	0.8&0.2	19.93	99.9997	15.8&0.2	0.31	0.0002	133.3&0.5	79.76	0.0001
γ "CD *	0.7&0.2	3.19	99.9977	-	-	-	76.7&0.5	96.81	0.0023
POPOP"γ"CD	0.8&0.1	3.24	99.9928	11.4&0.4	0.57	0.0061	111.4&0.4	96.19	0.0011

The aqueous solutions of CDs and POPOP"CDs were filtered with the 0.2" µm filter; c(POPOP)=2.5(10.6 mol L⁻¹, c(CD)=0.015 mol L⁻¹;

*taken from Ref.[13], c(CD)=0.01 mol L-1

[13] 注3XO, ~ MNX/tV7 XxY **2** POPOP () X β "CD F γ "CD } ~• \$ OV7 \$ | UV 才\$新X! x W1VFTUVXn 新\uXfg GHX,/ **新X\uO** POPOP () pq β"CD F γ"CD f g Xrst\u./n\.1 189<=>A<< =I_A<BCDE(X\. "Fn .

W 献[26]★ 【KL, 知 ● BD(XHIYz b_ 占(kk[POPOP"CDs V7 Y5D(占Xs ((^ 1), 1 W UVWrstXs ((0.0002%(POPOP" β "CD) **I** _ 0.0061% (POPOP" γ "CD).

p 值和温度对 POPOP- β - 纳米管的影响 键n . **OrstfgX**主V驱G P` n^[1"14]. N O POPOP () XA<BCDE POPOP" β "CD X} ~• pH %"Xhi. r , POPOP () X r **> E_** 碱 9a

XU; < 持"%. ~●碱EX! , **j** pH N 12 Xe候,r 骤xb 至 dX ./n xY^{POPOP} () $pqfgX\beta^{HCD}rst$ Hq 🖌 😑 12 X} ~• ?>?`. $j \sim \bullet X \, pH \quad O \mid \beta^{"}CD X \, pK_a , f \, 12.20 \, e^{[27]},$ 1 | β"CD () X s) ", s端XkRI %g **On**负离), e^β["]CD()^C Lfg 键,r 键[6X驱G("=fg. -. \ st * **]1** 献**\$E\]Yf**^[2,8'9,13].

9b **Ο** ΡΟΡΟΡ"β"CD **} ~ •** POPOP () XA<BCDE 96%"X 7.kl POPOP () X r ~ • 9bcde "%. (j9b N331Ke迅速b ./n\]^_+ POPOP''β"CD rst ~ • 9bd| 331 K I < X U; =?>?`,j9bj | 331Kerst 始瓦 . • rstX/nEs `9 X ()里**R\$**潜`X56价 () q



as a function of p a and temperature b mol •

结 论

89:; <= FG@<HIX-. \] ^_, POPOP() kl pq β "CD F γ "CD⁻} ~• f grst\u.?@A<X-. \] ^_, POPOP () ⁻ dabe1 β "CD fg1#2 Xhi ,⁻ j abekl mnopq β "CD F γ "CD fgrst \u.z| POPOP() ⁻ γ "CD } ~• XA<. !,01| POPOP() gzm2 γ "CD cOX3 4 ,@(⁻ γ "CD rst fg05R6i G HX.pH F9b: 5X-. \] ^_, POPOP() pq β "CD fgXrst,⁻ ~• XpH O| 12 F9bj | 331 K e" =?>?⁻.

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