Supporting Information

OEGylated Cyclodextrin-Based Thermoresponsive Polymers and Their Switchable Inclusion Complexation with Fluorescent Dyes

Qiongqin Mao, Kun Liu, Wen Li, Jiatao Yan,* and Afang Zhang*

Laboratory of Polymer Chemistry, Department of Polymer Materials, College of Materials Science and Engineering, Shanghai University, Materials Building Room 447, Nanchen Street 333, Shanghai 200444, China. E-mails: jiataoyan2006@gmail.com (J. Y.) or azhang@shu.edu.cn (A. Z.)
Table of Contents
Table S1. Polymerization condition and characterization of OEGylated CyD polymers.................. S3
Table S2. Apparent association constants (K_a) for the complexation of TNS with M-DEG and P-DEG at room temperature.................................................. S3
Figure S1. GPC elution curves of P-DEG and P-TEG.................................................. S3
Figure S2. Temperature varied ¹H NMR spectroscopy of P-DEG (a) and M-DEG (b) in D_2O.................................................................................. S4
Figure S3. (a) The unweighted size distributions of P-DEG in methanol and water below or above T_{cp}. (b) Plot of hydrodynamic radius (R_h) vs. temperature for 0.025 wt% aqueous solution of P-DEG.............................................................................. S4
Figure S4. Job plots for the complexes between TNS and M-DEG or P-DEG in water S5
Figure S5. Benesi-Hildebrand plots obtained from circular dichroism spectroscopy titrations of TNS with M-DEG (a) or P-DEG (b) at 20 °C.................................................. S5
Figure S6. Molecular structure of PG1...................................................................... S5
Figure S7. ¹H NMR spectra of TNS with different amounts of β-CyD in D_2O................. S6
Figure S8. Temperature varied ¹H NMR spectroscopy of the equivalent mixture of TNS and P-DEG.......................................................................................... S6
Figure S9. Dependence of θ_{317} for the complexes of TNS with M-DEG or P-DEG on solution temperature................................................................. S6
Figure S10. Temperature varied fluorescence spectra for the complex between P-DEG and TNS............................................................................... S7
Figure S11. (a) Temperature varied fluorescence spectra for the complex between P-TEG and TNS. (b) Plot of fluorescence intensity at λ = 426 nm vs. temperature for the complex between P-TEG and TNS.................................................. S7
Figure S12. Temperature varied fluorescence spectra for the complex between P-DEG and ANS.................................................................................. S7
Figure S13. ¹H NMR spectrum of 2a in CDCl_3................................................................ S8
Figure S14. ¹H NMR spectrum of 2b in CDCl_3................................................................ S8
Figure S15. ¹H NMR spectrum of M-DEG in CDCl_3.................................................. S9
Figure S16. ¹H NMR spectrum of 2c in CDCl_3.......................................................... S9
Figure S17. ¹H NMR spectrum of 2d in CDCl_3.......................................................... S10
Figure S18. ¹H NMR spectrum of M-TEG in CDCl_3.................................................. S10
Figure S19. ¹H NMR spectrum of P-DEG in CDCl_3.................................................. S11
Figure S20. ¹H NMR spectrum of P-TEG in CDCl_3.................................................. S11
Table S1. Polymerization condition and characterization of OEGylated CyD polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Polymerization conditions</th>
<th>GPC results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temperature / °C</td>
<td>time / h</td>
</tr>
<tr>
<td>P-DEG</td>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>P-TEG</td>
<td>80</td>
<td>30</td>
</tr>
</tbody>
</table>

Table S2. Apparent association constants ($K_a$) for the complexation of TNS with M-DEG and P-DEG at room temperature. $K_a^1$ is determined by circular dichroism spectroscopy titrations, while $K_a^2$ determined by fluorescence titrations.

<table>
<thead>
<tr>
<th>Hosts</th>
<th>$K_a^1 \times 10^{-3} / M^{-1}$</th>
<th>$K_a^2 \times 10^{-3} / M^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-DEG</td>
<td>1.24</td>
<td>2.42</td>
</tr>
<tr>
<td>P-DEG</td>
<td>1.28</td>
<td>3.64</td>
</tr>
</tbody>
</table>

Figure S1. GPC elution curves of P-DEG and P-TEG.
Figure S2. Temperature varied $^1$H NMR spectroscopy of **P-DEG** (a) and **M-DEG** (b) in D$_2$O.

Figure S3. (a) The unweighted size distributions of **P-DEG** in methanol and water below or above $T_{cp}$. (b) Plot of hydrodynamic radius ($R_h$) vs. temperature for 0.025 wt% aqueous solution of **P-DEG**.
Figure S4. Job plots for the complexes between TNS and M-DEG or P-DEG in water. \( \theta_{317} \) represents the signal intensity at \( \lambda = 317 \) nm. \([\text{TNS}] + [\text{Host}] = 0.4 \) mM.

Figure S5. Benesi-Hildebrand plots obtained from circular dichroism spectroscopy titrations of TNS with M-DEG (a) or P-DEG (b) at 20 \( ^\circ \)C. \( \Delta \theta_{319} \) represents the change of the signal intensity at \( \lambda = 319 \) nm. \([\text{TNS}] = 0.4 \) mM.

Figure S6. Molecular structure of PG1.
Figure S7. $^1$H NMR spectra of TNS with different amounts of $\beta$-CyD in D$_2$O.

Figure S8. Temperature varied $^1$H NMR spectroscopy of the equivalent mixture of TNS and P-DEG. [TNS] = 0.93 mM.

Figure S9. Dependence of $\theta_{317}$ for the complexes of TNS with M-DEG or P-DEG on solution temperature. [TNS] = 0.4 mM.
Figure S10. Temperature varied fluorescence spectra for the complex between P-DEG and TNS. [TNS] = 20 μM, [P-DEG] = 200 μM.

Figure S11. (a) Temperature varied fluorescence spectra for the complex between P-TEG and TNS. (b) Plot of fluorescence intensity at \( \lambda = 426 \text{ nm} \) vs. temperature for the complex between P-TEG and TNS. [TNS] = 20 μM, [P-TEG] = 200 μM.

Figure S12. Temperature varied fluorescence spectra for the complex between P-DEG and ANS. [ANS] = 20 μM, [P-DEG] = 200 μM.
Figure S13. $^1$H NMR spectrum of 2a in CDCl$_3$.

Figure S14. $^1$H NMR spectrum of 2b in CDCl$_3$. 
Figure S15. $^1$H NMR spectrum of M-DEG in CDCl$_3$.

Figure S16. $^1$H NMR spectrum of 2c in CDCl$_3$. 

59
Figure S17. $^1$H NMR spectrum of 2d in CDCl$_3$.

Figure S18. $^1$H NMR spectrum of M-TEG in CDCl$_3$. 
Figure S19. $^1$H NMR spectrum of P-DEG in CDCl$_3$.

Figure S20. $^1$H NMR spectrum of P-TEG in CDCl$_3$. 