New flexible molecular probes bearing dansyl and TEMPO moieties for host-guest interactions in solution and gels

Sorin Mocanu, a Iulia Matei,* a Anca Leonties,* a Victorita Tecuceanu, b Ana Maria Hanganu, b,c Zamfirica Minea, a Alina Stancu, a Elena Irina Popescu a and Gabriela Ionita* a

a “Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy, 202 Splaiul Independentei, Bucharest 060021, Romania. E-mails: ige@icf.ro; iuliamatei@icf.ro.

b Organic Chemistry Centre of the Romanian Academy, 202B Splaiul Independentei, 78100 Bucharest, Romania.

c Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, 90-92 Panduri, 050663 Bucharest, Romania
Fig. S1. Deconvolution of the fluorescence spectra of (A) DA_{1.7} and (B) DA_{1.7}T in water in the absence (1) and in the presence of β-CD at 10^{-3} M (2) and 10^{-2} M (3) concentrations.
Table S1. Position (λ, in nm) and relative area (A, in %) of the two fluorescence bands obtained by deconvolution of the emission spectra of DAₙ and DAₙT in the absence and in the presence of β-CD

<table>
<thead>
<tr>
<th>[β-CD] (M)</th>
<th>DAₙ</th>
<th></th>
<th></th>
<th></th>
<th>DAₙT</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ₁</td>
<td>A₁</td>
<td>λ₂</td>
<td>A₂</td>
<td>λ₁</td>
<td>A₁</td>
<td>λ₂</td>
<td>A₂</td>
</tr>
<tr>
<td>0</td>
<td>473</td>
<td>0.9</td>
<td>542</td>
<td>99.1</td>
<td>473</td>
<td>0.3</td>
<td>538</td>
<td>99.7</td>
</tr>
<tr>
<td>10⁻³</td>
<td>473</td>
<td>2.4</td>
<td>537</td>
<td>97.6</td>
<td>473</td>
<td>1.7</td>
<td>536</td>
<td>98.3</td>
</tr>
<tr>
<td>10⁻²</td>
<td>473</td>
<td>4.2</td>
<td>529</td>
<td>95.8</td>
<td>471</td>
<td>5.6</td>
<td>528</td>
<td>94.4</td>
</tr>
</tbody>
</table>
Fig. S2. Dependence of the normalized fluorescence emission of DA$_{1.8}$T probes on the cyclodextrin concentration. The solid lines represent the best fits according to eq. (3) for (A) DA$_{1.2}$T, (B) DA$_{1.3}$T, (C) DA$_{1.4}$T, (D) DA$_{1.5}$T, (E) DA$_{1.6}$T, (F) DA$_{1.7}$T, (G) DA$_{1.8}$T, (H) DA$_{1.10}$T, (I) DA$_{1.12}$T.
Fig. S3. Dependence of the rotational correlation time of DA<sub>1,n</sub>T probes on the cyclodextrin concentration.
NMR spectra of DA$_{1.3}$ and DA$_{1.3}$T (reduced with hydrazine) in the absence and in the presence of β-cyclodextrin

The NMR spectra of DA$_{1.3}$ and DA$_{1.3}$T (reduced with hydrazine) have been recorded in the absence and in the presence of β-CD in deuterated water and in DMSO. This allowed us to evidence the differences in chemical shifts of the proton signals assigned to the dansyl group. Unfortunately, the corresponding dual probe, DA$_{1.3}$T, is not soluble in deuterated water at concentrations that would allow us to record NMR spectra. While fluorescence and EPR measurements can be performed at concentrations of $\sim 10^{-6}$–$10^{-4}$ M, NMR measurements require higher concentrations of the probes ($\sim 10^{-2}$ M). Moreover, while the complex of DA$_{1.3}$ with β-CD is soluble in deuterated water, the solid complex of DA$_{1.3}$T separated from solution. Therefore, in this case both β-CD and DA$_{1.3}$T were in too low concentration in solution to record the NMR spectra.

For this reason, we recorded the NMR spectra in another polar solvent that solubilizes both DA$_{1.3}$T and the mixture DA$_{1.3}$T/β-CD. As can be noticed from Figs. S4, S5 and Tables S1, S2, chemical shifts in the NMR spectrum of the DA$_{1.3}$T/β-CD mixture are observed for protons of the dansyl group but not of the TEMPO moiety. This sustain our conclusion, based on fluorescence and EPR data, that the dansyl moiety is involved in the inclusion process.
Fig. S4. $^1$H-NMR spectra in D$_2$O of: A – β-cyclodextrin, B – DA$_{1,3}$; C - β-cyclodextrin + DA$_{1,3}$. 
Table S1. Chemical shifts of DA1.3 and β-CD protons in D₂O

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Chemical shifts of β-CD (ppm)</th>
<th>Chemical shifts of DA₁,₃ (ppm)</th>
<th>Chemical shifts of β-CD + DA₁,₃ (ppm)</th>
<th>Δδ =</th>
<th>ppm</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-b</td>
<td>-</td>
<td>8.23</td>
<td>8.25</td>
<td>0.02</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>H-c</td>
<td>-</td>
<td>7.68</td>
<td>7.70</td>
<td>0.02</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>H-d</td>
<td>-</td>
<td>8.49</td>
<td>8.57</td>
<td>0.08</td>
<td>40.3</td>
<td></td>
</tr>
<tr>
<td>H-f</td>
<td>-</td>
<td>7.41</td>
<td>7.38</td>
<td>0.03</td>
<td>17.2</td>
<td></td>
</tr>
<tr>
<td>H-g</td>
<td>-</td>
<td>7.70</td>
<td>7.74</td>
<td>0.05</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td>H-h</td>
<td>-</td>
<td>8.27</td>
<td>8.30</td>
<td>0.03</td>
<td>14.1</td>
<td></td>
</tr>
<tr>
<td>H-1</td>
<td>-</td>
<td>2.96</td>
<td>3.02</td>
<td>0.06</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>H-2</td>
<td>-</td>
<td>1.73</td>
<td>1.82</td>
<td>0.09</td>
<td>45.70</td>
<td></td>
</tr>
<tr>
<td>H-3</td>
<td>-</td>
<td>2.88</td>
<td>2.98</td>
<td>0.11</td>
<td>52.3</td>
<td></td>
</tr>
<tr>
<td>-N(CH₃)₂</td>
<td>-</td>
<td>2.86</td>
<td>2.88</td>
<td>0.02</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>H-2ꞌ</td>
<td>5.07</td>
<td>-</td>
<td>5.04</td>
<td>0.03</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>H-3ꞌ</td>
<td>3.58</td>
<td>-</td>
<td>3.56</td>
<td>0.02</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>H-4ꞌ</td>
<td>3.97</td>
<td>-</td>
<td>3.85</td>
<td>0.12</td>
<td>55.8</td>
<td></td>
</tr>
<tr>
<td>H-5ꞌ</td>
<td>3.90-3.85</td>
<td>-</td>
<td>3.79-3.72</td>
<td>0.11-0.13</td>
<td>57.5-64.8</td>
<td></td>
</tr>
<tr>
<td>H-6ꞌ</td>
<td>3.65</td>
<td>-</td>
<td>3.63</td>
<td>0.02</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>H-7ꞌ</td>
<td>3.90-3.85</td>
<td>-</td>
<td>3.79-3.72</td>
<td>0.11-0.13</td>
<td>57.5-64.8</td>
<td></td>
</tr>
</tbody>
</table>
Fig. S5. $^1$H-NMR spectra in DMSO of: A – β-cyclodextrin, B – DA$_{1,3}$T, C - β-cyclodextrin + DA$_{2,3}$T.
Table S2. Chemical shifts of DA_{1,3}T and β-CD protons in DMSO

| Compounds protons | Chemical shifts of β-CD (ppm) | Chemical shifts of DA_{1,3}T (ppm) | Chemical shifts of β-CD + DA_{1,3}T (ppm) | \( \Delta \delta = \left| \delta_{\text{BCD}} - \delta_{\text{DA}_{1,3}T} \right| \) |
|-------------------|-------------------------------|-----------------------------------|------------------------------------------|---------------------------------|
| H-b               | -                             | 8.08                              | 8.06                                     | 0.02                            | 9.6 |
| H-c               | -                             | 7.62-7.53                         | 7.64-7.55                                | 0.02                            | 9.4 |
| H-d               | -                             | 8.45                              | 8.43                                     | 0.02                            | 8.98 |
| H-f               | -                             | 7.25                              | 7.23                                     | 0.02                            | 9.7 |
| H-g               | -                             | 7.62-7.53                         | 7.64-7.55                                | 0.02                            | 9.4 |
| H-h               | -                             | 8.28                              | 8.26                                     | 0.02                            | 10.8 |
| H-1               | -                             | 2.93                              | 2.92                                     | 0.01                            | 6.7 |
| H-2               | -                             | 1.43                              | 1.40                                     | 0.03                            | 15.3 |
| H-3               | -                             | 2.74                              | 2.72                                     | 0.02                            | 9.6 |
| -N(CH_3)_{2}      | -                             | 2.82                              | 2.81                                     | 0.01                            | 6.2 |
| H-2''             | 4.83                          | -                                 | 4.82                                     | 0.01                            | 4.5 |
| H-3''             | 3.36-3.29                     | -                                 | Overlapped with water signal from DMSO | -                               | -   |
| H-4''             | 3.67-3.55                     | -                                 | 3.65-3.52                                | 0.02-0.03                       | 11.1-15.6 |
| H-5''             | 3.67-3.55                     | -                                 | 3.65-3.52                                | 0.02-0.03                       | 11.1-15.6 |
| H-6''             | 3.36-3.29                     | -                                 | Overlapped with water signal from DMSO | -                               | -   |
| H-7''             | 3.67-3.55                     | -                                 | 3.65-3.52                                | 0.02-0.03                       | 11.1-15.6 |
| -CH (TEMPO)       | -                             | 2.63                              | 2.63                                     | 0                                | 0.0 |
| -CH_2 (TEMPO)     | -                             | 1.74                              | 1.74                                     | 0                                | 0.0 |
| -CH_3 (TEMPO)     | -                             | 1.06 and 1.02                     | 1.055-1.015                              | 0.005                           | 1.6 |
Spectral characterization of DA\textsubscript{1,n}

Notation of H atoms for assignment of NMR \textsuperscript{1}H signals

\begin{align*}
\text{MAD-2, } n=2, \text{ -NH-CH}_{2}\text{-CH}_{2}\text{-NH}_{2} \\
\text{MAD-3, } n=3, \text{ -NH-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-NH}_{2} \\
\text{MAD-4, } n=4, \text{ -NH-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-NH}_{2} \\
\text{MAD-5, } n=5, \text{ -NH-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-NH}_{2} \\
\text{MAD-6, } n=6, \text{ -NH-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-NH}_{2}
\end{align*}
**DA_{1.2} (dansyl ethylenediamine)**

ESI-MS (m/z): 294 (DA_{1.2} + H^+)

ESI-MS (m/z): 292 (DA_{1.2} - H^+)
$^1$H NMR spectrum of compound DA$_{1,2}$
$^{13}$C NMR spectrum of compound DA$_{1.2}$

UV-Vis spectrum of compound DA$_{1.2}$
DA$_{1.3}$ (dansyl 1,3-diaminopropane)

ESI-MS ($m/z$): 308 (DA$_{1.3}$ + H$^+$)

ESI-MS ($m/z$): 306 (DA$_{1.3}$ - H$^+$)


\[ ^1H \text{ NMR spectrum of compound DA}_{1.3} \]
$^{13}$C NMR spectrum of compound DA$_{1.3}$

UV-Vis spectrum of compound DA$_{1.3}$
**DA$_{1.4}$ (dansyl 1,4-diaminobutane)**

**ESI-MS (m/z): 321 (DA$_{1.4}$ + H$^+$)**

**ESI-MS (m/z): 320 (DA$_{1.4}$ - H$^+$)**
$^1$H NMR spectrum of compound DA$_{1.4}$
$^{13}$C NMR spectrum of compound DA$_{1.4}$

UV-Vis spectrum of compound DA$_{1.4}$
DA$_{1.5}$ (dansyl 1,5-diaminopentane)

ESI-MS ($m/z$): 335 (DA$_{1.5}$ + H$^+$)

ESI-MS ($m/z$): 334 (DA$_{1.5}$ - H$^+$)
$^1$H NMR spectrum of compound DA$_{1,5}$
$^{13}$C NMR spectrum of compound DA$_{1.5}$

UV-Vis spectrum of compound DA$_{1.5}$
DA_{1.6} (dansyl 1,6-diaminohexane)

ESI-MS (m/z): 350 (DA_{1.6} + H^+)

ESI-MS (m/z): 348 (DA_{1.6} - H^+)
$^1$H NMR spectrum of compound DA$_{1.6}$
$^{13}$C NMR spectrum of compound DA$_{1.6}$

UV-Vis spectrum of compound DA$_{1.6}$
DA$_{1.7}$ (dansyl 1,7-diaminoheptane)

ESI-MS ($m/z$): 364 (DA$_{1.7}$ + H$^+$)

ESI-MS ($m/z$): 362 (DA$_{1.7}$ - H$^+$)
$^1$H NMR spectrum of compound DA$_{1.7}$
$^{13}$C NMR spectrum of compound DA$_{1.7}$

UV-Vis spectrum of compound DA$_{1.7}$
**DA_{1.8}** (dansyl 1,8-diaminoctane)

ESI-MS ($m/z$): 378 (DA_{1.8} + H^+)

ESI-MS ($m/z$): 376 (DA_{1.8} - H^+)
$^1$H NMR spectrum of compound DA$_{1.8}$
$^{13}$C NMR spectrum of compound DA$_{1.8}$

UV-Vis spectrum of compound DA$_{1.8}$
DA_{1.10} (dansyl 1,10-diaminodecane)

ESI-MS (m/z): 406 (DA_{1.10} + H^+)

ESI-MS (m/z): 404 (DA_{1.10} - H^+)
$^1$H NMR spectrum of compound DA$_{1.10}$
$^{13}$C NMR spectrum of compound DA$_{1.10}$

UV-Vis spectrum of compound DA$_{1.10}$
$DA_{1.12}$ (dansyl 1,12-diaminododecane)

ESI-MS ($m/z$): 434 ($DA_{1.12} + H^+$)

ESI-MS ($m/z$): 432 ($DA_{1.12} - H^+$)
$^1$H NMR spectrum of compound DA$_{1.12}$
$^{13}$C NMR spectrum of compound DA$_{1.12}$

UV-Vis spectrum of compound DA$_{1.12}$
Spectral characterization of $\text{DA}_{1,n}\text{T}$

$\text{DA}_{1.2}\text{T}$

ESI-MS ($m/z$): 474 ($\text{DA}_{1.2}\text{T} - \text{H}^+$)

UV-Vis spectrum of compound $\text{DA}_{1.2}\text{T}$
EPR spectrum of $\text{DA}_{1.5}\text{T}$
DA$_{1.3}$T

ESI-MS (m/z): 488 (DA$_{1.3}$T - H$^+$)

UV-Vis spectrum of compound DA$_{1.3}$T
EPR spectrum of DA_{1.3}T
DA$_{1.4}$T

ESI-MS (m/z): 502 (DA$_{1.4}$T - H$^+$)

UV-Vis spectrum of compound DA$_{1.4}$T
EPR spectrum of DA$_{1.4}$T
DA$_{1.5}$T

ESI-MS (m/z): 516 (DA$_{1.5}$T - H$^+$)

UV-Vis spectrum of compound DA$_{1.5}$T
EPR spectrum of DA$_{1.5}$T
ESI-MS (m/z): 530 (DA_{1.6}T - H^+)

UV-Vis spectrum of compound DA_{1.6}T
EPR spectrum of DA$_{1.5}$T
DA$_{1.7}$T

ESI-MS ($m/z$): 544 (DA$_{1.7}$T - H$^+$)

UV-Vis spectrum of compound DA$_{1.7}$T
EPR spectrum of DA_{1.7}T
DA_{1.8} T

ESI-MS (m/z): 558 (DA_{1.8} T - H^+)

UV-Vis spectrum of compound DA_{1.8} T
EPR spectrum of DA$_{1.8}$T
**DA_{1.10}T**

**ESI-MS (m/z):** 586 (DA_{1.10}T - H^+)

**UV-Vis spectrum of compound DA_{1.10}T**
EPR spectrum of DA$_{1.10}$T
**DA$_{1.12}$T**

ESI-MS ($m/z$): 615 (DA$_{1.12}$T)

UV-Vis spectrum of compound DA$_{1.12}$T
EPR spectrum of DA$_{1.12}$T