Electronic Supplementary Information


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I. Additional $^1$H NMR Spectra

Fig. S1. $^1$H NMR spectra of 1 (b), 2 (c) and 3 (d) in DMSO-$d_6$. The $^1$H NMR spectrum of 4 in DMSO-$d_6$ is reported for comparison (a). The asterisked peaks refer to -CH=CH$_2$ signals of the 4-(undec-10-enoxy) chains.
Fig. S2. Comparison of $^1$H NMR spectra of 4 (a), 4·BrTBA (b), 1·BrTBA (c) and 2 (d) in DCM-$d_2$. The asterisked peaks refer to -CH=CH$_2$ signals of the 4-(undec-10-enyloxy) chains of 4. The addition of BrTBA to a DCM-$d_2$ solution of 4 results in a sizable down-field shift of H$_3$ and H$_5$ signals, in agreement with the deaggregation process and formation of the 4·BrTBA adduct.$^1$
Fig. S3. $^1$H NMR spectra of 3 in DMSO-$d_6$ (a) and DCM-$d_2$ (b).
II. Additional Optical Absorption and Fluorescence Spectra

Fig. S4. UV/vis absorption spectra of 1 (−) and 2 (−) (1.0 × 10⁻⁵ M solutions) in DCM.
**Fig. S5.** UV/vis absorption and fluorescence ($\lambda_{\text{exc}} = 487$ nm) spectra of 1·BrTBA (−) and 2 (−) (1.0 × 10$^{-5}$ M solutions) in DCM.

**Fig. S6.** UV/vis absorption and fluorescence ($\lambda_{\text{exc}} = 470$ nm) spectra of 3 (1.0 × 10$^{-5}$ M) in DCM (−), THF (−) and DMSO (−).
**Fig. S7.** UV/vis absorption and fluorescence ($\lambda_{exc} = 479$ nm) spectra of 1 and 2 ($1.0 \times 10^{-5}$ M solutions) in DMSO.

**Fig. S8.** UV/vis absorption and fluorescence ($\lambda_{exc} = 428$ nm) spectra of 1 and 2 ($1.0 \times 10^{-5}$ M solutions) in THF.
III. DOSY NMR Data and Estimation of the Molecular Mass

We have used DOSY as independent method to estimate the molecular mass of the species present in solution.\textsuperscript{2} However, the non-spherical nature of the involved molecules does not allow any straightforward application of the Stokes-Einstein equation, as normally used to estimate the molecular size through the measurement of the diffusion coefficient, $D$.\textsuperscript{3} Thus, to achieve reliable molecular masses from DOSY measurements, we have chosen to estimate them by using a known internal reference species thus obtaining the molecular mass by their relative diffusion coefficient.\textsuperscript{4,5}

The molecular mass in solution, $m$, was simply estimated using Graham’s law of diffusion: 

\[ D = K \left( \frac{T}{m} \right)^{1/2} \]

where the constant $K$ depends on geometric factors, including the area over which the diffusion is occurring. By assuming a constant temperature and that $K$ is the same for both species in solution, the relative diffusion rate of two species A and B is given by: 

\[ D_A/D_B = (m_B/m_A)^{1/2} \]

This allows the calculation of an unknown molecular mass by eq. 1:

\[ m_B = m_A \left( \frac{D_A}{D_B} \right)^2 \quad (S1) \]

Therefore, the diffusion rate values obtained by DOSY can be used to estimate the molecular mass of a species, by comparison with the actual $D$ value of a known internal reference (e.g., the solvent).\textsuperscript{4b,5}

A representative 2D DOSY plot of 2 is shown in Fig. S9. It is important to note that peaks from molecules with different diffusion rates appear in different positions on the y-axis (diffusion rate) and can easily be assigned to each molecule. Using the cursor in VNMRJ, in the case of 2 in DCM-d\textsubscript{2} maxima were found corresponding to $D = 36.00 \times 10^{-10}$ m$^2$ s$^{-1}$, for the solvent,\textsuperscript{6} and $D = 9 \times 10^{-10}$ m$^2$ s$^{-1}$, for the complex (Fig. S9). The $^1$H signal in DCM-d$\textsubscript{2}$ is related to CCl$_2$HD, with a molecular mass of 85.941 Da. Therefore, using these data and applying eq. S1 a mass of 1375.06 Da is calculated, in agreement with the presence of a dimeric species (1464.12 Da) in solution.
Fig. 9. $^1$H NMR DOSY spectrum of 2 in DCM-d$_2$.

References