Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

DNA nanotubes and helical nanotapes via self-assembly of ssDNA-amphiphiles

Timothy R. Pearce[a] and Efrosini Kokkoli[*b]

[a]Department of Biomedical Engineering, University of Minnesota,
Minneapolis, MN, 55455, USA.
[b]Department of Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, MN, 55455, USA.

Corresponding author:
Efrosini Kokkoli
Tel: +16126261185, fax: +16126267246
Email: kokkoli@umn.edu

Table S1 Liquid chromatography-mass spectroscopy data of the 10, 25, and 40 nucleotide (nt) ssDNA-amphiphiles created with or without a C_{12} spacer and various headgroups, as shown in Fig. 1.

		No Spacer		C_{12} Spacer	
		Expected Mass (M-H)	Oberved Mass (M-H)	Expected Mass (M-H)	Oberved Mass (M-H)
NoG headgroups	10nt-1	3,801.1	3,799.6	3,998.5	3,997.1
	10nt-2	3,834.2	3,832.6	4,031.6	4,030.0
	25nt	8,364.1	8,361.7	8,561.5	8,559.4
	40nt	12,930.1	12,927.2	13,127.5	13,127.5
G_5 headgroups	10nt-1	3,932.2	3,930.9	4,129.6	4,128.3
	10nt-2	3,980.2	3,979.4	4,177.6	4,176.3
	25nt	8,495.2	8,493.0	8,692.6	8,690.0
	40nt	13,061.1	13,058.5	13,258.5	13,255.3
$(GGGT)_3$ headgroups	25nt	8,631.2	8,630.9		
	40nt	13,197.2	13,196.9		

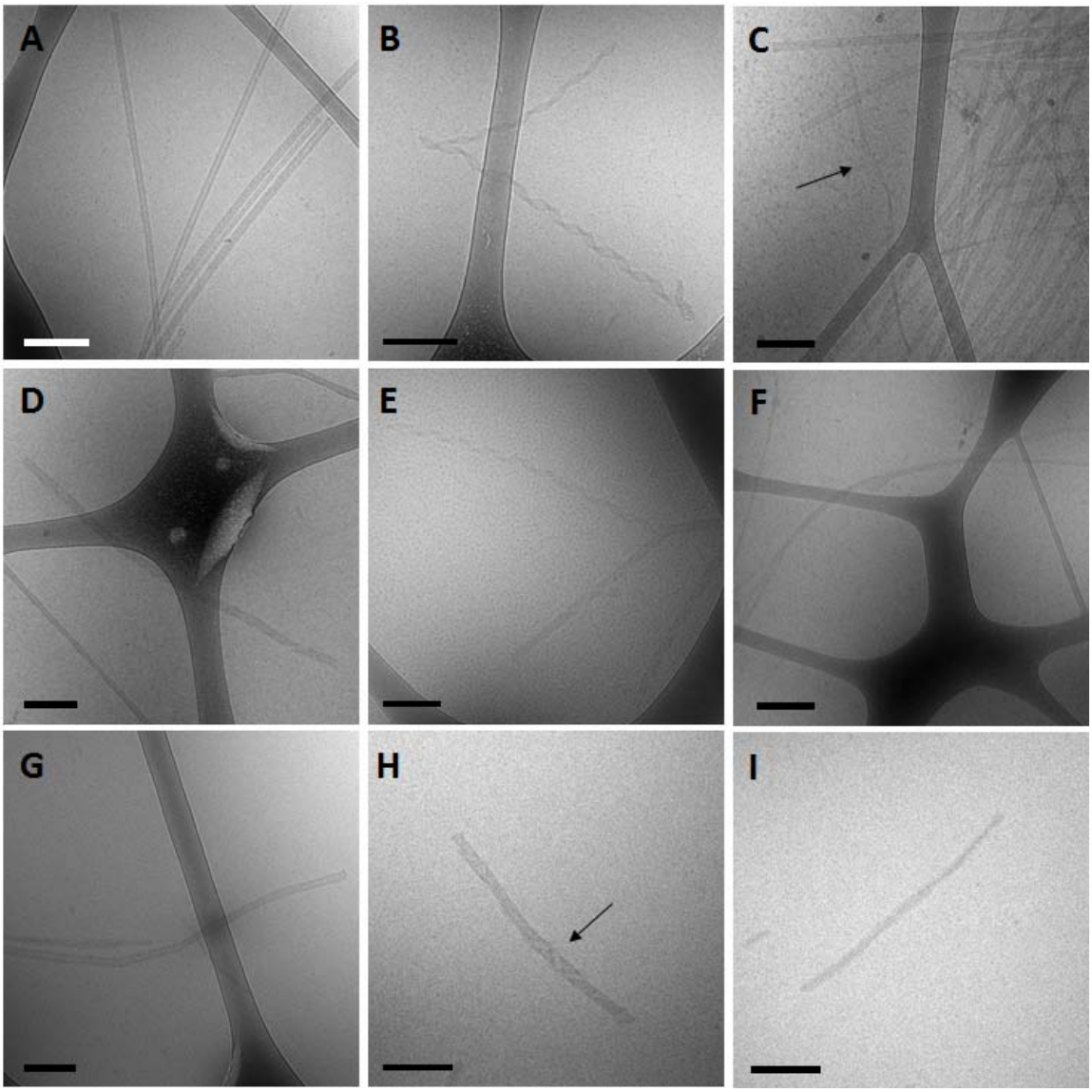

Fig. S1 Cryo-TEM images of nanotubes (A, D, G), helical nanotapes (B, E, H), and twisted nanotapes (C, F, I) formed by ssDNA-amphiphiles with guanine-free (NoG) headgroups and C_{12} spacers. Top row: (A, C) 10nt-1 headgroup, (B) 10nt-2 headgroup. Middle row (D, E, F): 25nt headgroup. Bottom row (G, H, I): 40nt headgroup. The black arrow in C shows the twisted nanotape structure, and in H a helical section of the nanostructure. All scale bars are 200 nm.

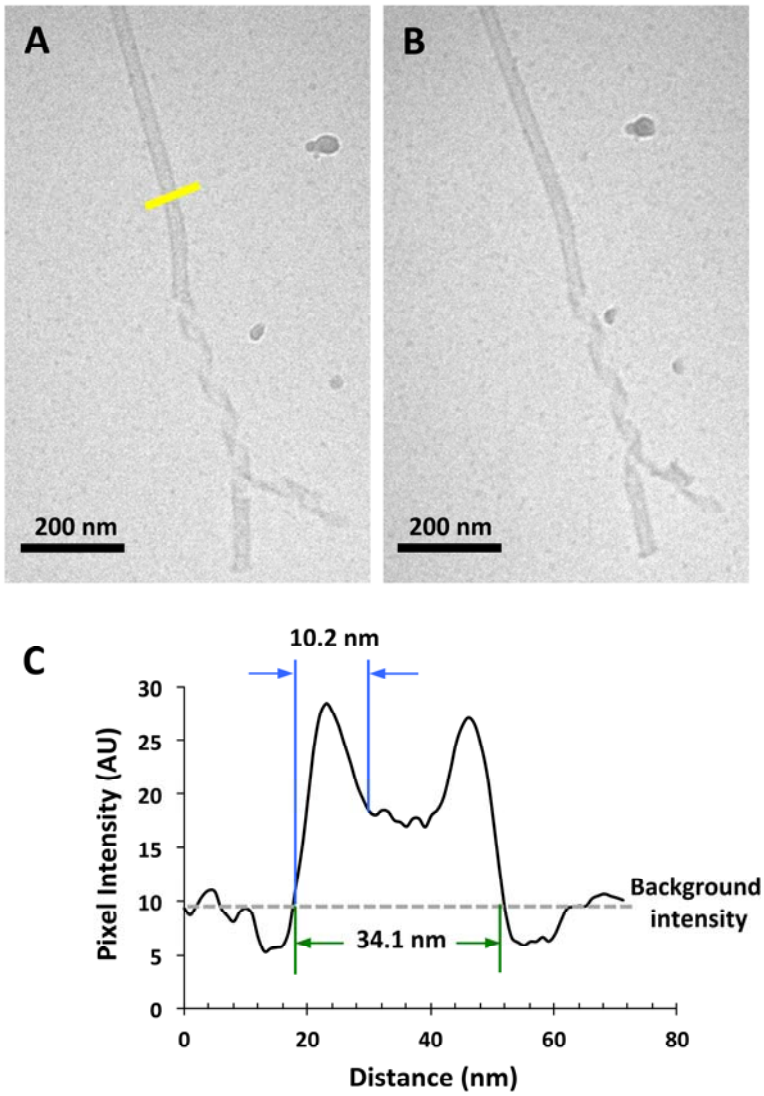

Fig. S2 Cryo-TEM and line-scan analysis of ssDNA-amphiphiles with a 25 nucleotide NoG headgroup and a C_{12} spacer. Images of the same nanotube and helical nanotape section A) before and after B) a 45° stage tilt. The diameter of the nanotube segment at 0° and 45° tilt is 34 nm. C) Line-scan analysis of a segment of the untilted cryo-TEM image (yellow line in A) shows the characteristic shape of a hollow cylinder, 34 nm in diameter with 10 nm thick walls, confirming the cylindrical structure observed in the sample is a nanotube.

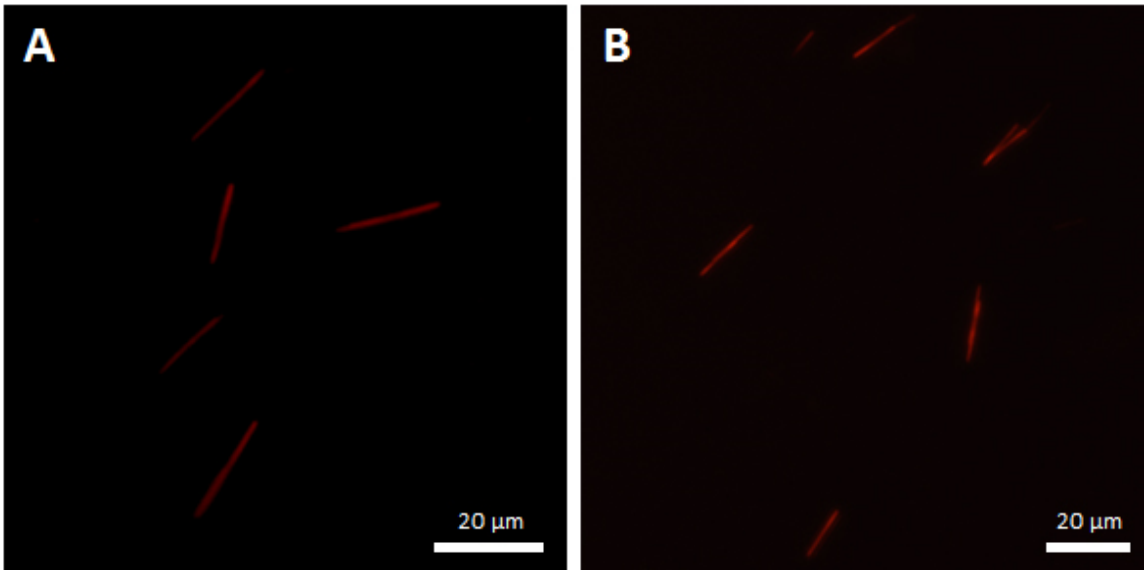

Fig. S3 Fluorescent images of high aspect ratio structures formed by amphiphiles with the C_{12} spacer and guanine-free (NoG) headgroups A) 10 nucleotides (10nt-1) or B) 40 nucleotides in length. Amphiphile samples were stained with the hydrophobic Nile red dye prior to imaging.

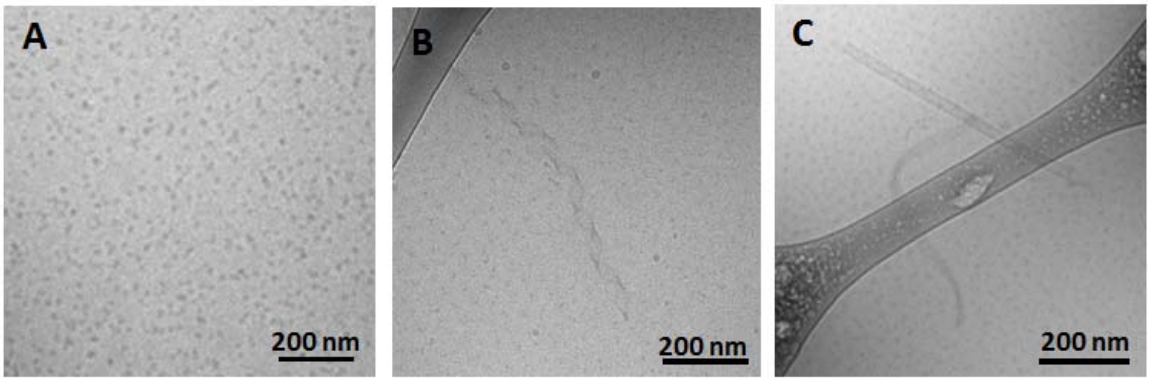

Fig. S4 Cryo-TEM images of A) micelles formed by ssDNA-amphiphiles with a 10 nucleotide (10nt-1) G_5-modified headgroup lacking the C_{12} spacer (NoSPR), B) a helical nanotape and C) a twisted nanotape and nanotube formed by ssDNA-amphiphiles with the 40nt G_5-modified headgroup and without the C_{12} spacer (NoSPR).

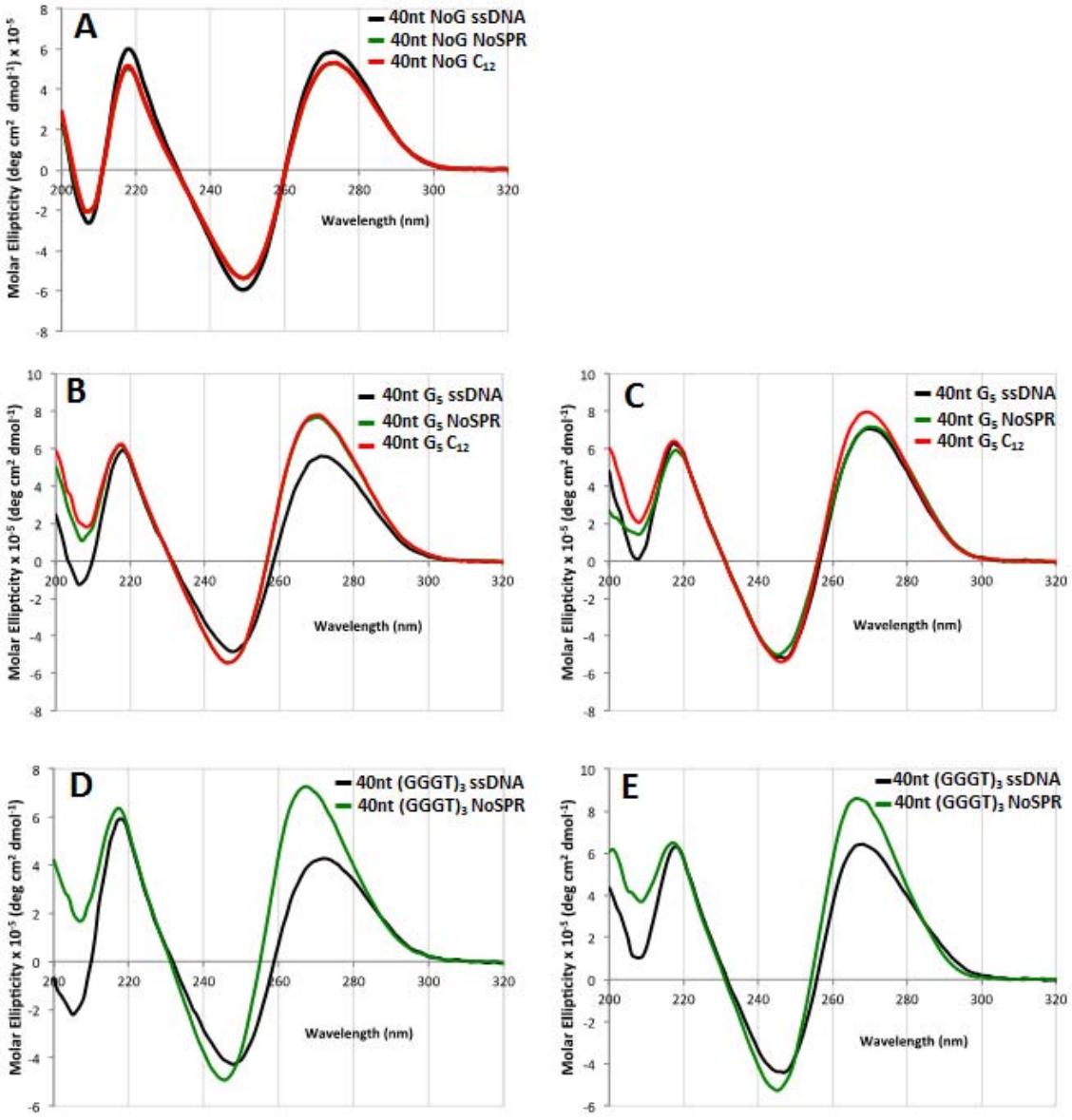

Fig. S5 CD spectra in Milli-Q water (A, B, D) or 20 mM KCl (C, E) of 20 µM solutions of free ssDNA with 40nt NoG, G_5-, or $(GGGT)_3$-modified sequences and their amphiphiles with (C_{12}) and without (NoSPR) the C_{12} spacer.

Table S2 Summary of cryo-TEM (Fig. S1, S4, S7, S8) and circular dichroism (CD) observations (Fig. S5) from amphiphiles containing 40 nucleotide (nt) headgroups in Milli-Q water or 20 mM KCl. The location of the long wavelength maximum in each CD spectrum was used to assign headgroup structure. Maxima occurring between 258-265 nm were assigned as G-quadruplex, between 270-285 nm were assigned as stem-loop, and between 266-269 nm were assigned as unclear.

Sample	High aspect ratio structures	CD maximum (nm) in H_2O/KCl	Headroup assignment
40nt NoG ssDNA	-	273	Stem-loop
40nt NoG NoSPR	No	273	Stem-loop
40nt NoG C_{12}	Yes	274	Stem-loop
40nt G_5 ssDNA	-	271/269	Stem-loop/Unclear
40nt G_5 NoSPR	No	270/269	Stem-loop/Unclear
40nt G_5 C_{12}	Yes	270/269	Stem-loop/Unclear
40nt $(GGGT)_3$ ssDNA	-	272/267	Stem-loop/Unclear
40nt $(GGGT)_3$ NoSPR	Yes	267/267	Unclear/Unclear

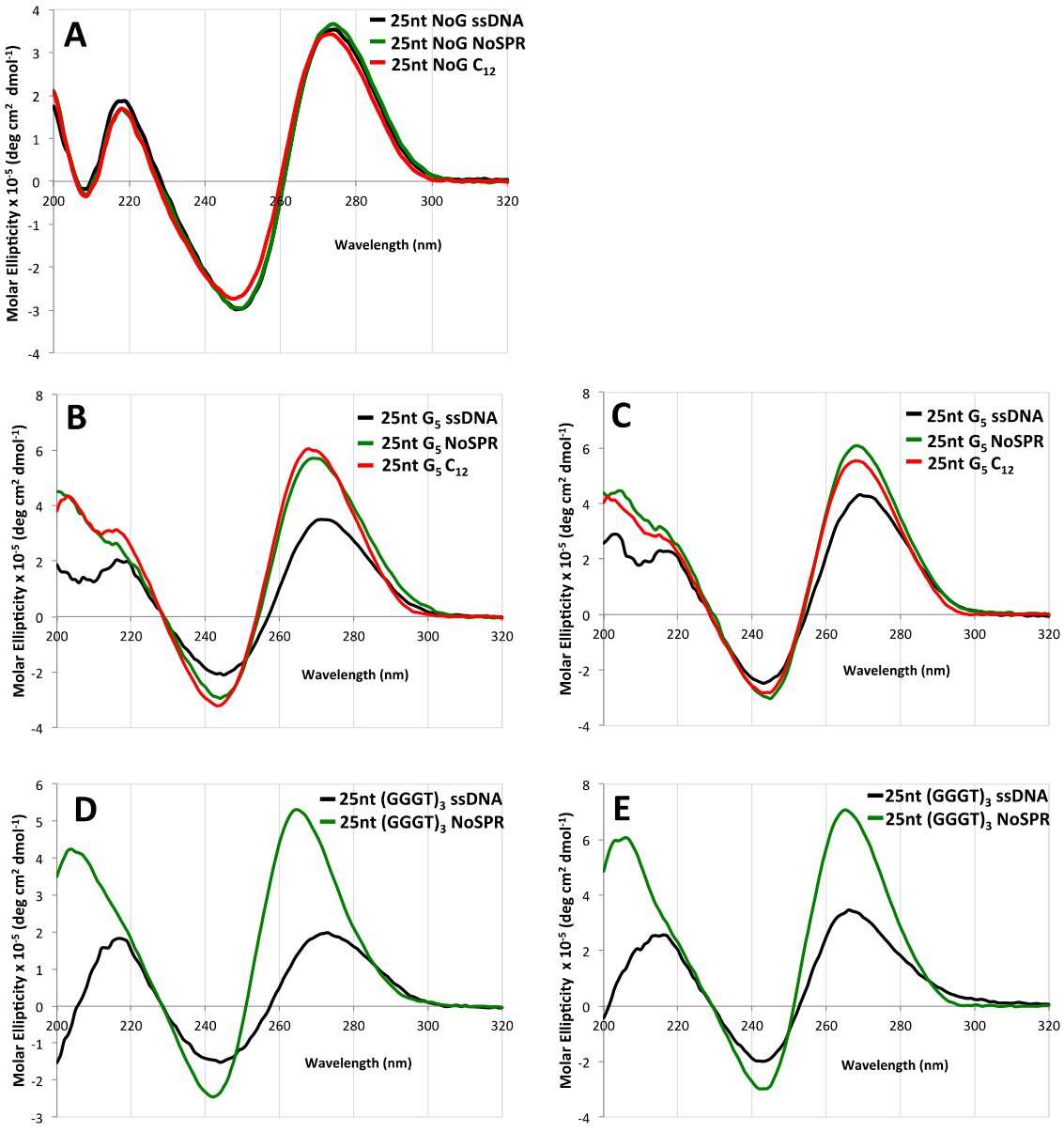

Fig. S6 CD spectra in Milli-Q water (A, B, D) or 20 mM KCl (C, E) of 20 µM solutions of free ssDNA with 25nt NoG, G_5-, or $(GGGT)_3$-modified sequences and their amphiphiles with (C_{12}) or without (NoSPR) the C_{12} spacer.

Table S3 Summary of cryo-TEM (Fig. S1, S2, S7, S8) and circular dichroism (CD) observations (Fig. S6) from amphiphiles containing 25 nucleotide (nt) headgroups in Milli-Q water or 20 mM KCl. The location of the long wavelength maximum in each CD spectrum was used to assign headgroup structure. Maxima occurring between 258-265 nm were assigned as G-quadruplex, between 270-285 nm were assigned as stem-loop, and between 266-269 nm were assigned as unclear.

Sample	High aspect ratio structures	CD maximum (nm) in H_2O/KCl	Headroup assignment
25nt NoG ssDNA	-	274	Stem-loop
25nt NoG NoSPR	No	274	Stem-loop
25nt NoG C_{12}	Yes	273	Stem-loop
25nt G_5 ssDNA	-	272/269	Stem-loop/Unclear
25nt G_5 NoSPR	No	269/268	Unclear/Unclear
25nt G_5 C_{12}	Yes	268/269	Unclear/Unclear
25nt $(GGGT)_3$ ssDNA	-	273/266	Stem-loop/Unclear
25nt $(GGGT)_3$ NoSPR	Yes	265/265	G-quad/G-quad

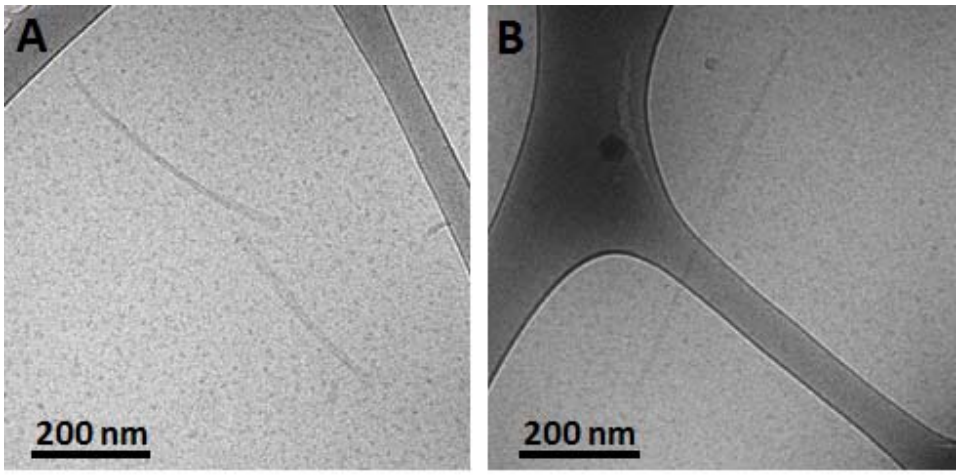

Fig. S7 Cryo-TEM images of twisted nanotapes formed by ssDNA-amphiphiles with the A) 25nt $(GGGT)_3$-modified headgroup or B) 40nt $(GGGT)_3$-modified headgroup and without the C_{12} spacer (NoSPR).

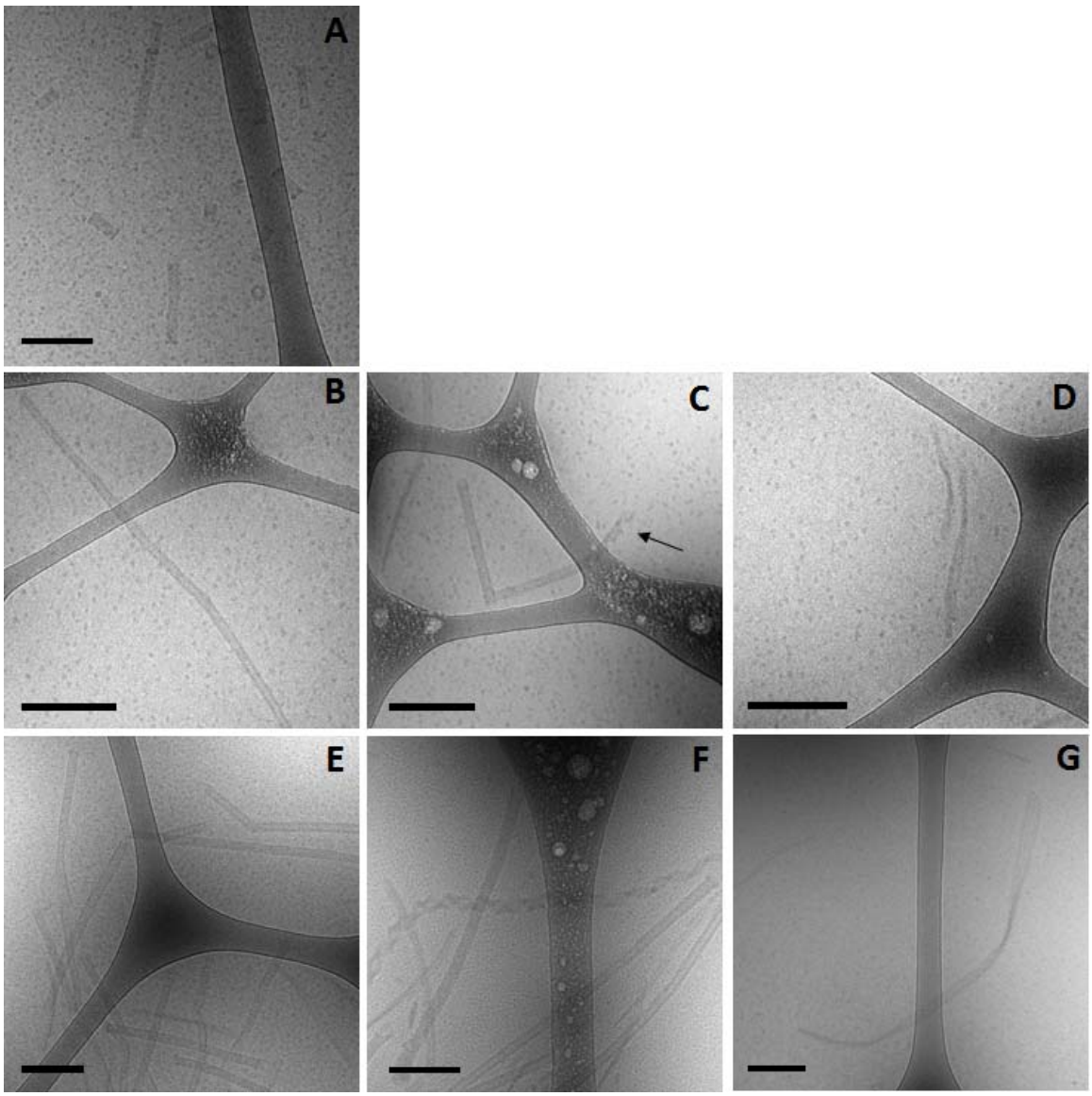

Fig. S8 Cryo-TEM images of nanotubes (A, B, E), helical nanotapes (C, F), and twisted nanotapes (D, G) formed by ssDNA-amphiphiles with G_5-modified headgroups and C_{12} spacers. Top row (A): 10nt-1 headgroup. Middle row (B, C, D): 25nt headgroup. Bottom row (E, F, G): 40nt headgroup. The black arrow in C shows the helical section of the nanostructure. All scale bars are 200 nm.

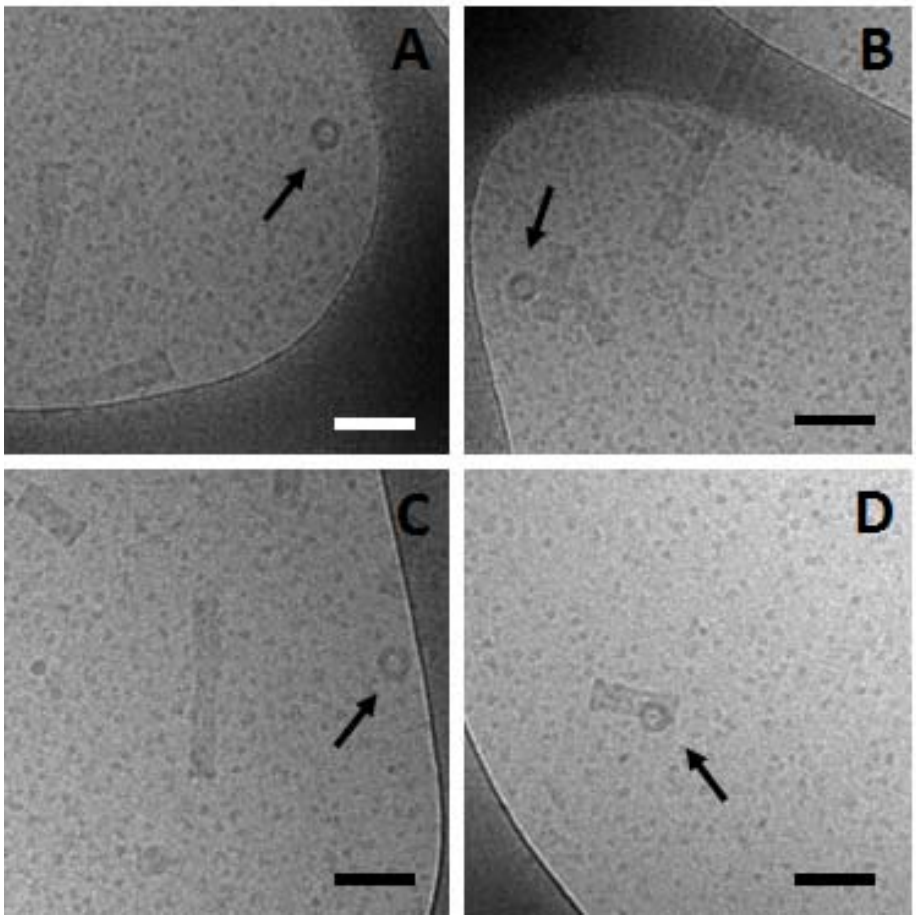

Fig. S9 Cryo-TEM images of short nanotubes (A-D) formed by the amphiphiles with the 10nt-1 G_5-modified headgroup, and the C_{12} spacer. The black arrows point to nanotubes that are viewed end-on, demonstrating the hollow nature of these structures. All scale bars are 100 nm.

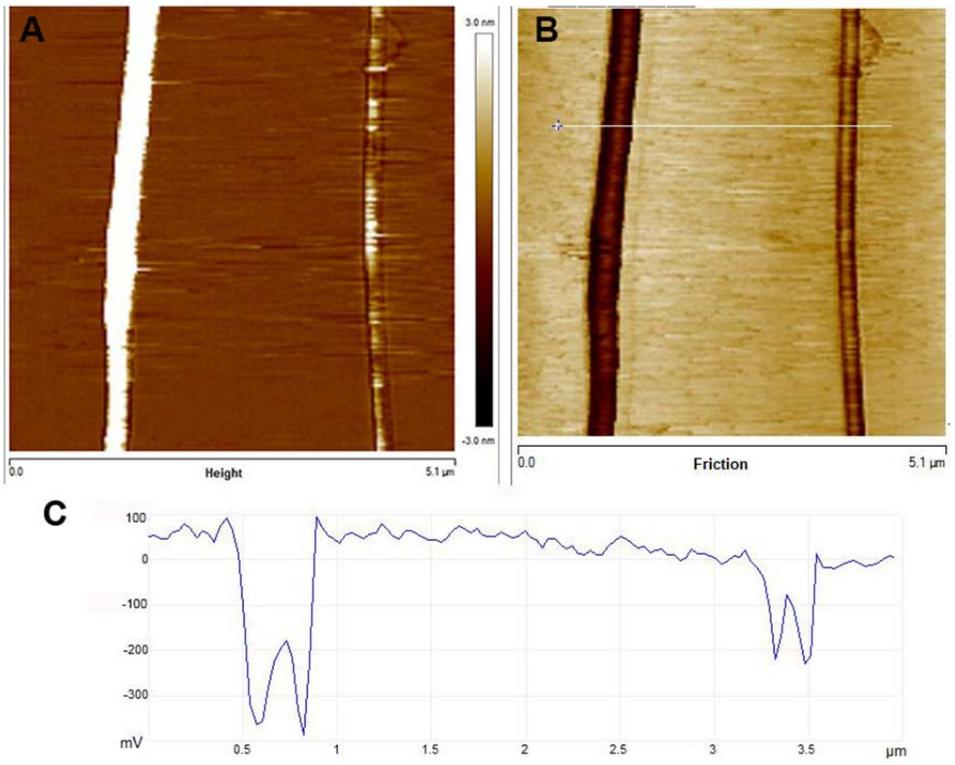

Fig. S10 AFM images and line-scan analysis of nanotubes formed by amphiphiles containing the 25 nucleotide G_5-modified headgroup and the C_{12} spacer. A) Height image. B) Friction image. C) Line-scan analysis of the white line shown in B. Friction imaging can map relative differences in surface frictional characteristics, thus allowing the identification of surface features that may not be clear in height imaging. Friction imaging and line-scan analysis on the friction image shows the presence of four nanotubes.

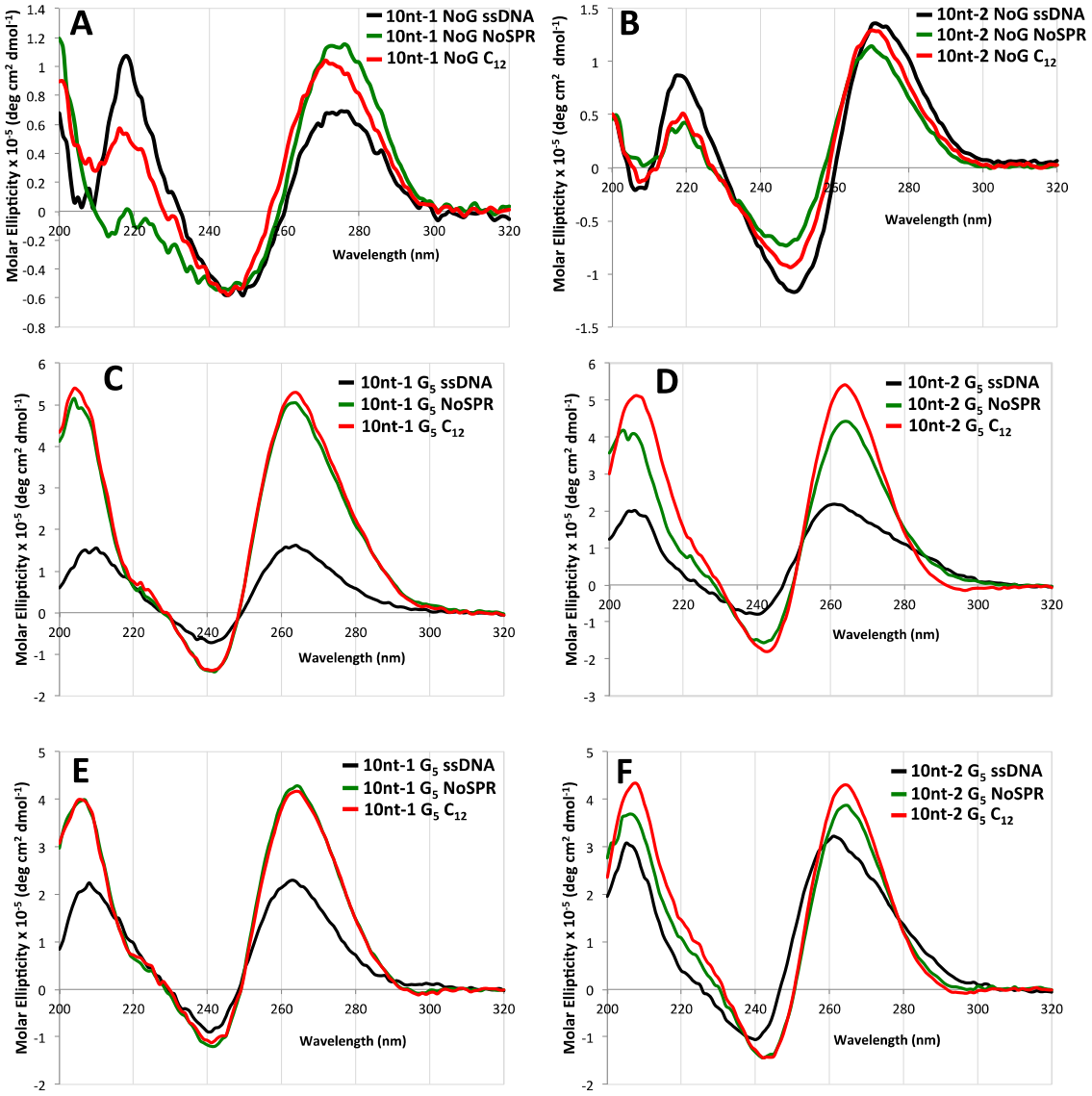

Fig. S11 CD spectra in Milli-Q water (A-D) or 20 mM KCl (E, F) of 20 µM solutions of free ssDNA with 10nt NoG or G_5-modified headgroups and their amphiphiles with (C_{12}) and without (NoSPR) the C_{12} spacer.

Table S4 Summary of cryo-TEM (Fig. S1, S2) and circular dichroism (CD) observations (Fig. S11) from amphiphiles containing 10 nucleotide (nt) headgroups in Milli-Q water or 20 mM KCl. The location of the long wavelength maximum in each CD spectrum was used to assign headgroup structure. Maxima occurring between 258-265 nm were assigned as G-quadruplex, between 270-285 nm were assigned as stem-loop, and between 266-269 nm were assigned as unclear.

Sample	High aspect ratio structures	CD maximum (nm) in H_2O/KCl	Headroup assignment
10nt-1 NoG ssDNA	-	275	Stem-loop
10nt-1 NoG NoSPR	No	276	Stem-loop
10nt-1 NoG C_{12}	Yes	271	Stem-loop
10nt-2 NoG ssDNA	-	271	Stem-loop
10nt-2 NoG NoSPR	No	270	Stem-loop
10nt-2 NoG C_{12}	Yes	270	Stem-loop
10nt-1 G_5 ssDNA	-	264/263	G-quad/G-quad
10nt-1 G_5 NoSPR	No	263/264	G-quad/G-quad
10nt-1 G_5 C_{12}	Yes	264/264	G-quad/G-quad
10nt-2 G_5 ssDNA	-	261/261	G-quad/G-quad
10nt-2 G_5 NoSPR	No	264/264	G-quad/G-quad
10nt-2 G_5 C_{12}	Yes	264/264	G-quad/G-quad

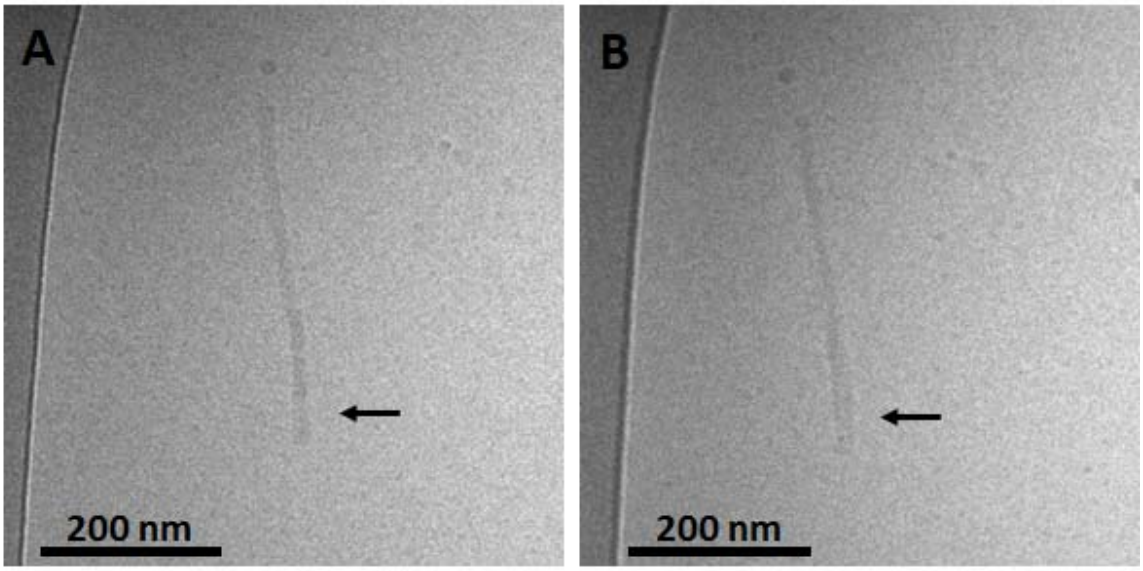

Fig. S12 Cryo-TEM images of 25 nucleotide G_5-modified amphiphiles containing the C_{12} spacer after 2 days of aging at room temperature following thermal disruption. A) 0° stage tilt. B) 45° stage tilt. The visual change in width of the nanostructure following the stage tilt, most easily observed at the location indicated by the black arrows, demonstrates that the nanostructure is a bilayer nanotape rather than a cylindrical micelle.

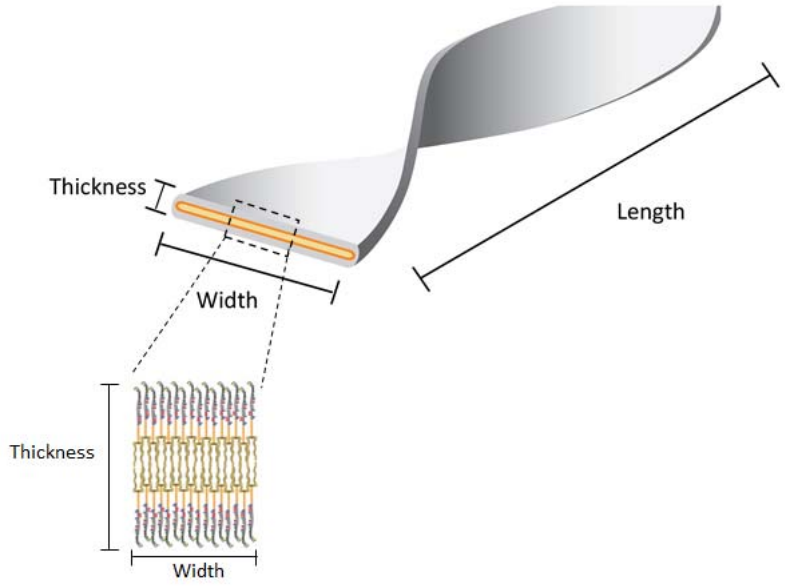

Fig. S13 An artistic rendering of the self-assembly of ssDNA-amphiphiles into a bilayer nanotape structure. The thickness, width, and length dimensions of the nanotape are identified for clarity.

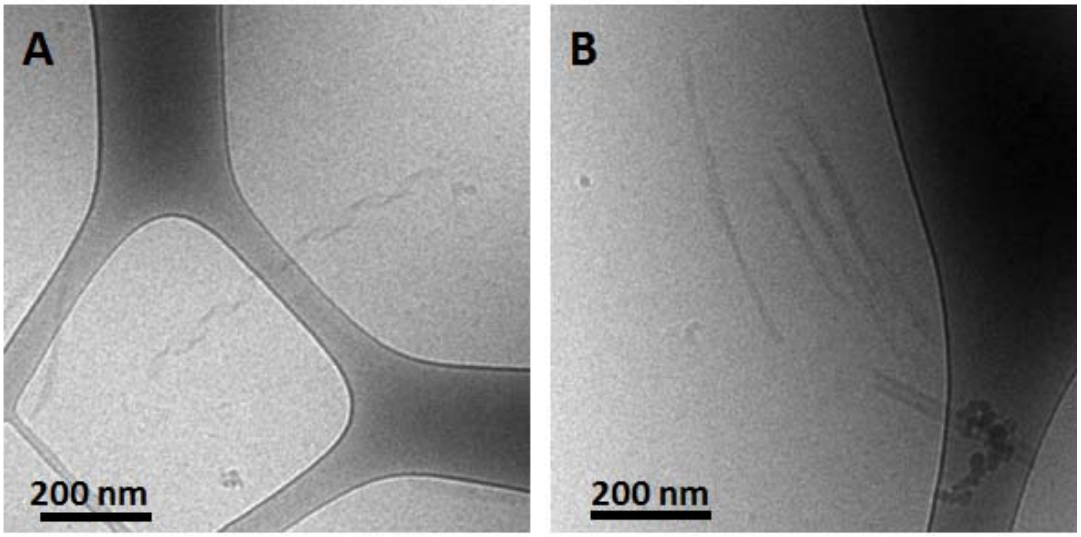

Fig. S14 Cryo-TEM images of ssDNA-amphiphiles containing a 25 nucleotide NoG headgroup and the C_{12} spacer after 6 months of aging at room temperature.