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Light-induced disassembly of self-assembled vesicle-capped nanotubes observed in real time

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Molecular self-assembly is the basis for the formation of numerous artificial nanostructures^{1,2}. The self-organization of peptides^{3–6}, amphiphilic molecules composed of fused benzene rings^{7–10} and other functional molecules^{11–15} into nanotubes is of particular interest. However, the design of dynamic, complex self-organized systems that are responsive to external stimuli remains a significant challenge¹⁶. Here, we report self-assembled, vesicle-capped nanotubes that can be selectively disassembled by irradiation. The walls of the nanotubes are 3-nm-thick bilayers and are made from amphiphilic molecules with two hydrophobic legs that interdigitate when the molecules self-assemble into bilayers. In the presence of phospholipids, a phase separation between the phospholipids and the amphiphilic molecules creates nanotubes, which are end-capped by vesicles that can be chemically altered or removed and reattached without affecting the nanotubes. The presence of a photoswitchable and fluorescent core in the amphiphilic molecules allows fast and highly controlled disassembly of the nanotubes on irradiation, and distinct disassembly processes can be observed in real time using fluorescence microscopy.

A key feature of nature's complex multifunctional self-assembled objects is that they are dynamic and show adaptability in response to external stimuli. Therefore, to push the frontiers of self-assembly¹⁷, it is important to create structures of high complexity that can also be made to change in terms of structure, composition or properties by accommodating responsive functions into the system^{18–23}. We have developed a complex, light-responsive, self-assembled nanotube system based on a photochemically active amphiphilic monomer unit (Fig. 1). This molecule was designed to enable light-induced switching, while also having the ability to assemble into uniform and stable nanotubes. Phospholipid vesicles readily assemble onto these nanotubes to form unique end-capped hybrid systems. The nanotube-vesicle complex can then be altered either by selective and reversible detachment of the cap from the tube (Fig. 1, Path 1) or by light-triggered disassembly of the nanotubes (Fig. 1, Path 2). The photochemically induced disassembly process can be precisely controlled, and can be followed in real time using confocal and epifluorescence microscopy.

The structure of amphiphile **1** combines a photosensitive overcrowded alkene unit with hydrophilic oligoethylene glycol head groups and hydrophobic alkyl tails (Fig. 2a; see Supplementary Information for synthesis and characterization of **1**). The core unit provides a photoreactive and fluorescent functionality, and the oligoethylene glycol units allow for dispersion in water. A special design feature of amphiphile **1** is the presence of two precisely positioned hydrophobic legs that allow bilayer formation by

means of interdigitation of the opposing amphiphilic molecules in the bilayer (Fig. 2d). We have previously shown that the core unit is photoactive^{24,25}. As a result of steric hindrance between the upper and lower halves of the overcrowded alkene core, the weakly blue fluorescent compound **1** adopts an *anti*-folded structure (Fig. 2a). Ultraviolet irradiation of **1** ($\lambda = 365$ nm) at room temperature results in the formation of cyclized compound **2**, indicated by the generation of a new absorption band at 470 nm (Fig. 2b) and a new intense green emission band at 535 nm with concomitant loss of the emission at 435 nm (Fig. 2c). The formation of **2** can be achieved following irradiation at wavelengths shorter than 406 nm and was confirmed by ¹H-NMR spectroscopy and mass spectrometry studies (see Supplementary Information).

Under aqueous conditions, amphiphile **1** spontaneously self-assembles to generate nanotubes with low aspect ratios (Fig. 2f). Phospholipid 1,2-dioleoyl-*sn*-glycero-3-phosphate (DOPC) was added to improve the solubility of the amphiphile. This addition of phospholipids resulted in micrometre-long nanotube structures, the aspect ratios of which could be controlled by the ratio of amphiphile **1**:DOPC. However, to our surprise, a phase separation between amphiphile **1** and DOPC also led to the formation of unique nanotubes capped with DOPC vesicles (Fig. 2g,i). By investigating different amphiphile/lipid ratios, a 2:1 amphiphile/DOPC ratio was found to give tubes with the highest aspect ratio (500) and uniformity of tubular structure of $\sim 10 \mu\text{m} \times 28$ nm (Fig. 2g) with a tube-wall diameter of 3 nm (Fig. 2e, red bar). It should be emphasized that the vesicle-capped nanotubes (Fig. 2i) have two distinct bilayers: the 3 nm nanotube wall comprising amphiphile **1**, and the thicker vesicle wall with a 4 nm DOPC bilayer. (For other amphiphile/DOPC ratios see Supplementary Chart S1; for accompanying differential scanning calorimetry (DSC) measurements, see Supplementary Figs S1 and S2). The bilayer thickness was measured on slightly defocused cryo-electron microscopy images to obtain maximal phase contrast. The highest density was obtained from the electron-dense overcrowded alkene part of the amphiphile²⁷. The bilayer diameter is in agreement with that obtained from Hyperchem modelling studies for a perfectly interdigitated system (Fig. 2d,e). We attribute the high stability of the self-assembled structures to the specific interdigitation of the hydrophobic moieties of **1**, maximizing hydrophobic effects and van der Waals interactions between the alkyl chains, with additional stability from π -stacking of the arene moieties. Comparison of the electronic absorption spectra of amphiphile **1** in solution with that of the nanotubes indicates a redshift of the 294 nm absorption band to 298 nm (Supplementary Fig. S3). This bathochromic shift is indicative of π -stacking following self-assembly. In addition, the

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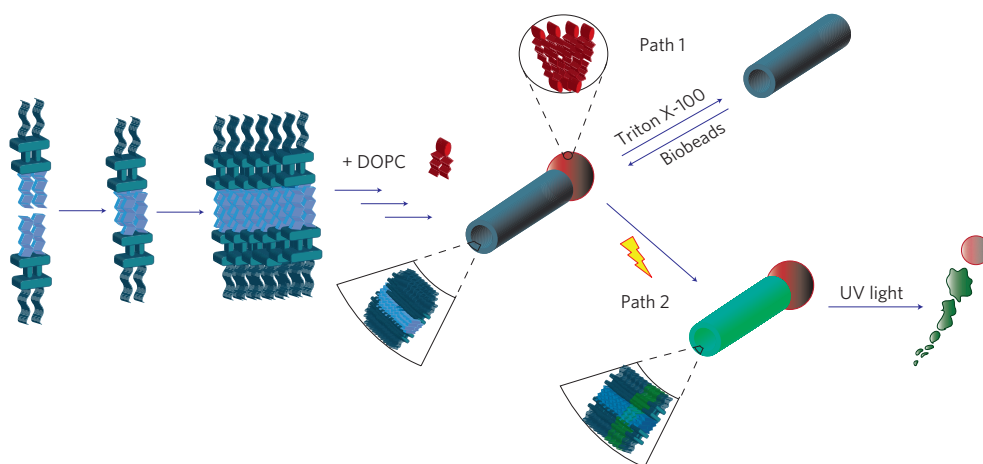


Figure 1 | Schematic representation of assembly and disassembly of vesicle-capped nanotubes. Self-assembly of a photochemically active amphiphile initially forms interdigitated bilayers followed by nanotube formation and capping of the nanotube with DOPC vesicles. Path 1: Treatment of vesicle-capped nanotubes with detergent (Triton X-100) dissolves the phospholipid capping vesicle without affecting the nanotube. Subsequent removal of detergent with Biobeads followed by freeze-thaw cycles regenerates the vesicle-capped nanotubes. Path 2: Irradiation leads to cyclization within the bilayer (signified here by a colour change from blue to green), eventually resulting in an intensity- and wavelength-dependent tube disassembly process. Real-time observation of the disassembly process shows distinct processes based on irradiation source or tube composition.

infrared spectrum of the nanotubes showed CH_2 stretching vibrations at 2,960, 2,921 and 2,852 cm^{-1} , attributed to stretched alkyl chains in an interdigitated system⁷ (Supplementary Fig. S5).

Although both tubes and vesicle caps are obtained by self-assembly of small amphiphilic molecules, the tubes were shown to be remarkably robust as a consequence of the specific nature of the bilayer organization. This provides the intriguing option for the capped vesicles to be changed or detached without affecting the nanotubes. We were pleased to find that the phospholipid cardiolipin also favourably interacted with amphiphile **1**, providing nanotubes capped with cardiolipin vesicles. Because cardiolipin is sensitive to the presence of divalent metal cations such as Ca^{2+} , treatment of cardiolipin vesicle-capped nanotubes with CaCl_2 before vitrification resulted in a change in phase of the appended vesicle from lamellar to the cubic/hexagonal phase (Fig. 2h). There was no indication of a change in nanotube structure due to the phase transition in the pendant vesicle. This indicates that the vesicles end-capping the nanotubes remain chemically reactive in an orthogonal fashion to that of the nanotube itself.

We also investigated the possibility of removing and reattaching the vesicle caps. The surfactant Triton X-100 is known for its ability to solubilize amphiphilic bilayers into mixed micelles by opening up the bilayer structure. Subsequent bilayer reformation can be achieved following removal of the Triton X-100²⁸. Indeed, the addition of small amounts of Triton X-100 to the DOPC end-capped tubes (Fig. 3a) resulted in the immediate release of the vesicles from the tubes. A further increase in detergent concentration completely dissolved the DOPC vesicles, but left the highly stable, interdigitated amphiphile **1** based tubes unaffected, reminiscent of membrane rafts²⁹ (Fig. 3b). Following Triton X-100 removal using Biobeads, DOPC vesicles were reformed via open membrane structures (Fig. 3c). Complete surfactant removal followed by freeze-thaw cycles enabled vesicle reattachment on the hydrophobic alkyl chains that are exposed to the aqueous medium at the end of the tube (Fig. 3d).

We next studied the effect of irradiation on the morphology of the self-assembled nanotube system, because we envisioned that photochemical cyclization of the core unit of the amphiphilic molecule would affect its geometry and the ability of the π -arene units to stack. The inherent emissive properties of amphiphile **1** as well as the distinct differences in the emission spectra of the *anti*-folded form **1** (blue fluorescent) and the cyclized form **2** (green

fluorescent) (Fig. 2c) allow for the conformational, spectroscopic as well as morphological changes within the nanotubes to be monitored simultaneously in real time.

Following ultraviolet irradiation ($\lambda = 390$ nm) the nanotubes were observed (using epifluorescence microscopy) to undergo a disassembly process, eventually forming aggregates (Fig. 4a–d). Tubular disassembly took place within seconds following irradiation at 390 nm (Supplementary Movie S1), and the rate and nature of this process was strongly dependent on the wavelength and intensity of the light used. Up to 15 min of irradiation at 488 nm caused no observable change in tubular morphology. Furthermore, monitoring the light-triggered disassembly process using confocal microscopy confirmed that it is induced by the formation of cyclized structure **2** (Fig. 3e,f). When a selected cross-section of a nanotube was monitored during irradiation it was shown that the blue emission ($\lambda_{\text{exc}} = 406$ nm, $\lambda_{\text{em}} = 435$ nm) associated with the *anti*-folded isomer **1** decreased, whereas the green fluorescence ($\lambda_{\text{exc}} = 494$ nm, $\lambda_{\text{em}} = 535$ nm) due to cyclized compound **2** increased in intensity (Fig. 3f). The dramatic enhancement of the 535 nm emission band was accompanied by structural changes within the tube (Fig. 3e), eventually leading to tube disassembly. These changes can be rationalized in terms of disruption of the bilayer due to conversion of *anti*-folded amphiphile molecules **1** to the more rigid cyclized form **2**. Notably, pure cyclized amphiphile **2** did not form nanotubes, but instead generated vesicles both in the presence and absence of a phospholipid (such as DOPC) (Supplementary Figs S7, S8). This again suggests that the change in geometry and rigidity introduced in the amphiphile by cyclization of **1** inhibits tube formation.

Cyclization of amphiphile **1** within the nanotubes leads to disassembly; to visualize the synchronous morphological changes, this process was monitored in parallel using absorption/fluorescence spectroscopy and cryo-transmission electron microscopy (cryo-TEM). A 200 μl suspension of nanotubes (2:1 amphiphile/DOPC) in water was irradiated at fixed time intervals at 400.8 nm. Monitoring the absorption and emission spectra of this sample over time indicated the generation of new bands associated with **2**, the product of cyclization of amphiphile **1** (Supplementary Fig. S9), with cryo-TEM images of the same samples at these time points indicating gradual changes in the morphology of the nanotubes (Fig. 3g). Before irradiation, typically capped nanotubes with diameters of 28 nm and lengths >10 μm are observed.

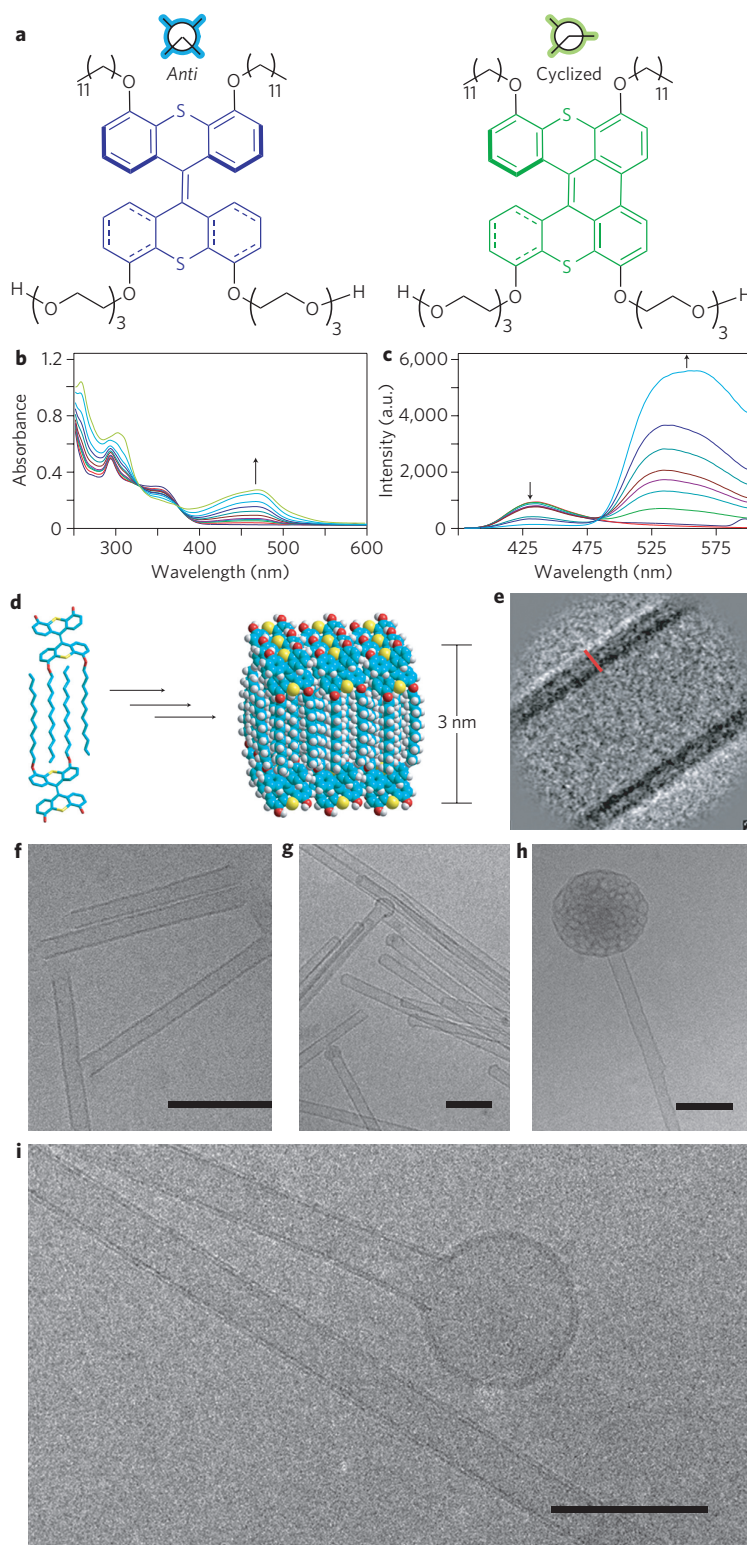


Figure 2 | Structure and properties of amphiphilic switch 1 and self-assembled nanotube morphologies. **a**, Molecular structure of *anti*-folded isomer **1** (blue) and cyclized compound **2** (green). **b,c**, Change in absorption (**b**) and emission (**c**) spectra over time with irradiation of **1** ($\lambda = 365$ nm) at room temperature in dichloromethane. **d**, Amber forcefield²⁶ calculated molecular model of the bilayer structure (PEG moieties are omitted from calculations). C, cyan; O, red; H, white; S, yellow. Interdigitated alkyl chains suggest an outer S-outer S distance of ~ 3 nm. Oligoethylene glycol units are omitted. **e**, Summed cryo-TEM images of a cross-section of the amphiphile nanotubes. Dark regions are bilayer walls. Red bar indicates an approximate thickness of 3 nm. **f-i**, Cryo-TEM images of self-assembled nanotubes generated by amphiphile **1** under aqueous conditions in the absence or presence of phospholipid. Scale bars, 100 nm. **f**, Low-aspect-ratio nanotubes generated from pure amphiphile **1** in the absence of DOPC. **g**, Micrometre-long vesicle-capped nanotubes obtained from a 2:1 amphiphile **1**/DOPC mixture. **h**, Nanotubes capped with cardiolipin showing a change in phase behaviour of the appended cardiolipin vesicle (from lamellar to cubic/hexagonal phase) in the presence of CaCl_2 . **i**, Expansion of amphiphile nanotubes capped with DOPC vesicles illustrating the two distinct bilayers of tube and vesicle.

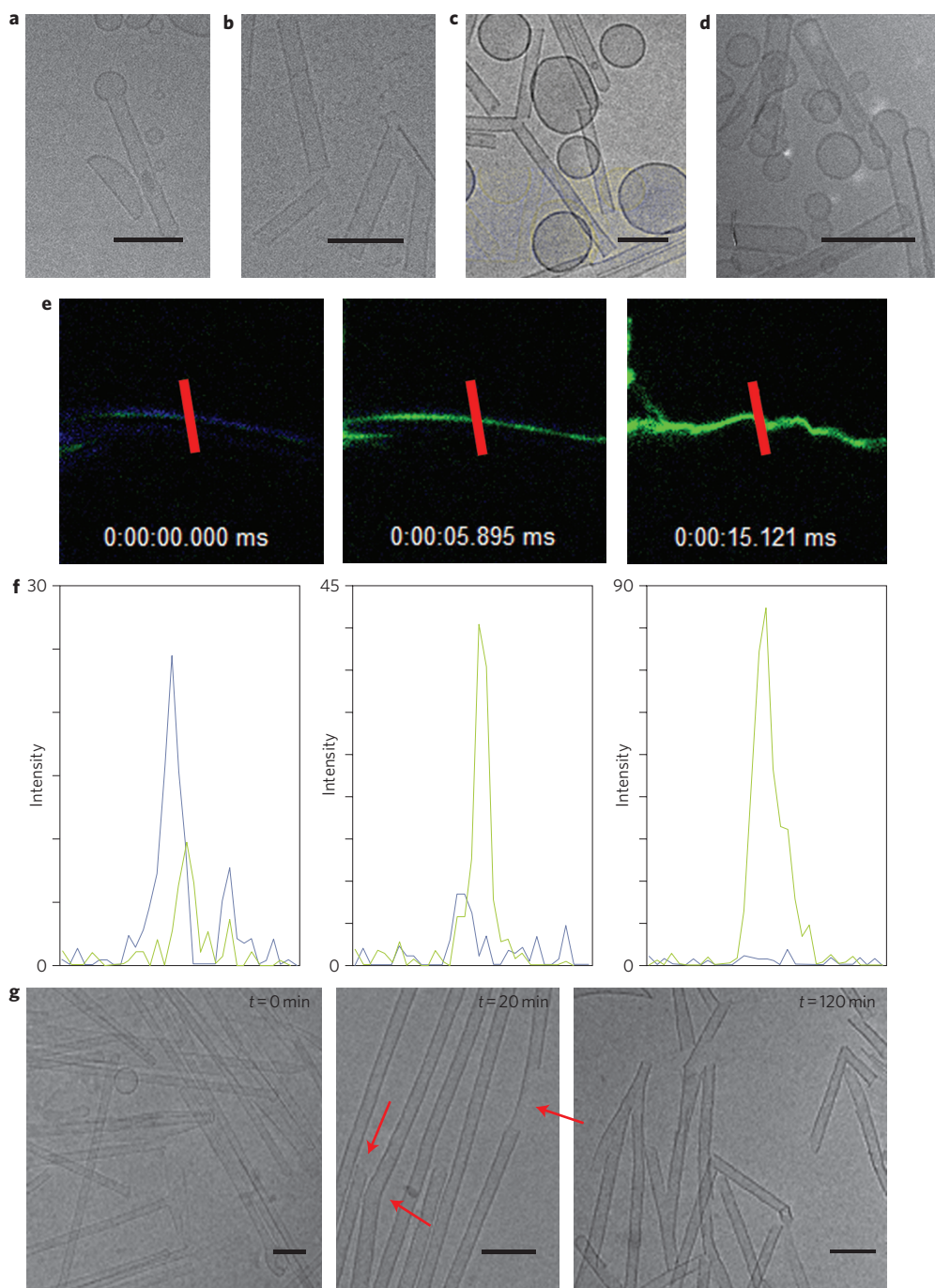


Figure 3 | Analysis of changes to morphology. **a–d**, Effect of addition of detergent Triton X-100 on DOPC-capped amphiphile nanotubes (1:1 amphiphile 1/DOPC). **a**, 0 mg ml⁻¹ of Triton X-100. **b**, 1.6 mg ml⁻¹ Triton X-100 – DOPC. Vesicles are completely solubilized, but nanotubes remain intact. **c**, Triton X-100 is completely removed using Biobeads, and DOPC vesicles are concomitantly regenerated. **d**, DOPC vesicles are reattached to the nanotubes after a freeze-thaw cycle. Scale bars, 100 nm. **e,f**, Confocal fluorescence microscopy images of the self-assembled tubes (**e**) with emission profiles (**f**, red line in **e**) as a function of time. Blue corresponds to emission intensity at an excitation wavelength of 406 nm, and green corresponds to emission intensity at an excitation wavelength of 494 nm. **g**, Cryo-TEM images demonstrating structural changes observed within the amphiphile nanotubes under laser irradiation at a wavelength of 400.8 nm. Cryo-TEM images were taken at $t = 0$ min, 20 min and 120 min. Red arrows indicate the formation of kinks and loss of large sections of the nanotube bilayer. Scale bars, 100 nm.

However, after 20 min of irradiation, many of the DOPC vesicles are no longer attached, kinks are observed and, importantly, sections of the nanotube bilayer wall are no longer present (indicated by the red arrows in Fig. 3g, $t = 20$ min). Extended irradiation for 2 h resulted in complete loss of the DOPC capping vesicles and the observation of only short, irregularly shaped nanotubes, finally leading to complete disassembly.

An attractive feature of the system is the level of control that can be achieved over the disassembly process of the nanotubes with a photochemical event through variation of the intensity or wavelength of light or through the use of photoactive dopants. For instance, irradiation at 365 nm instead of 390 nm (*vide supra*) using lower-intensity ultraviolet light resulted in a slower disassembly process and a concomitant change in morphology from tubes to

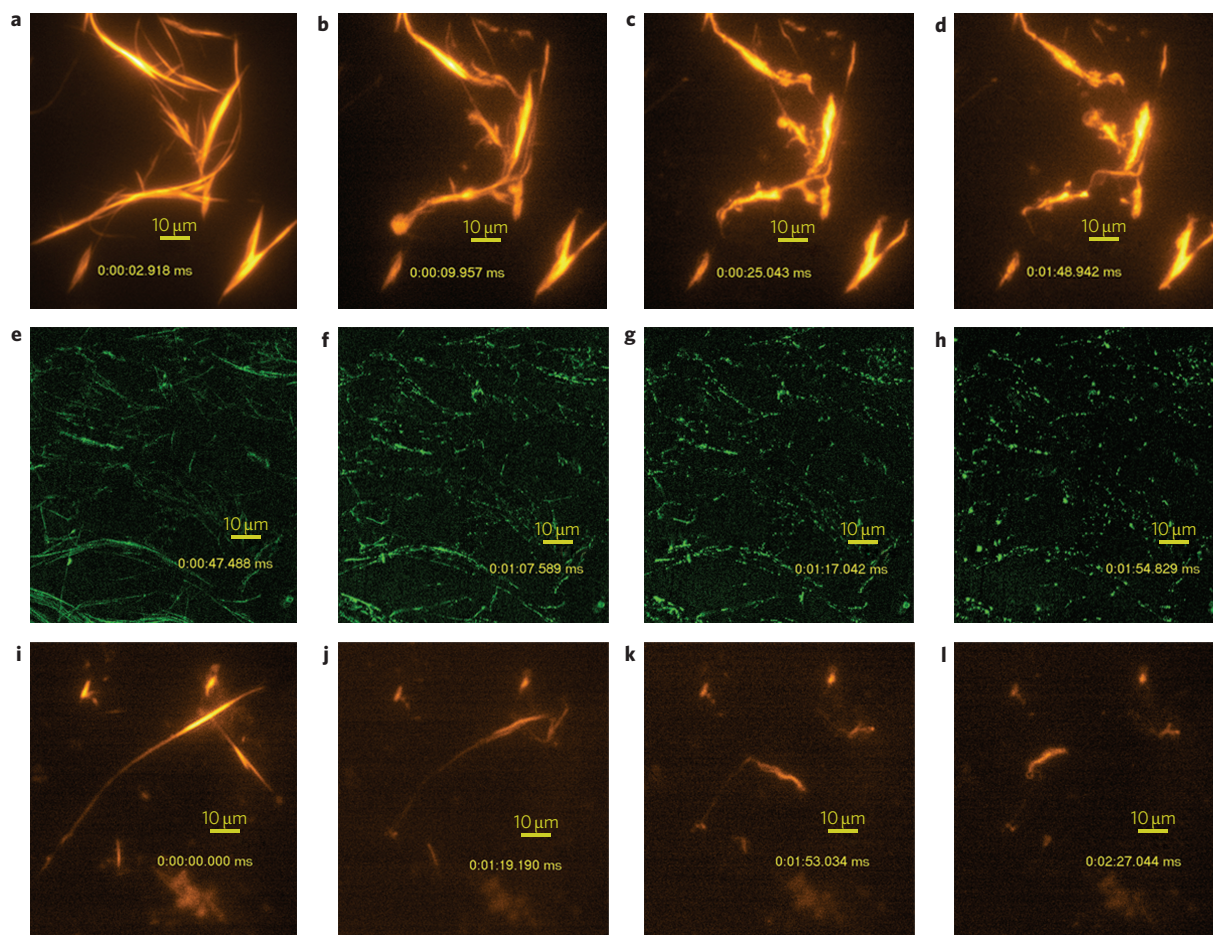


Figure 4 | Images of changes in tubular morphology as a function of time. **a–d**, Irradiation of tubes at 390 nm on an epifluorescence microscope. Tube composition, amphiphile 1:DOPC 2:1. Disassembly begins immediately and is complete after 25 s (**c**), forming large aggregates. **e–h**, Tube composition as in **a–d**, with low-intensity ultraviolet light ($\lambda = 365$ nm) as the irradiation source. Tube degradation commences after 45 s of irradiation and continues for almost 2 min, leaving behind small vesicle-like morphologies. **i–l**, Tubes consisting of amphiphile 1:DOPC:DiO (2:1:0.05) are observed bending and coiling in response to light in a process that takes ~ 2.5 min under the same irradiation conditions as in **a–d**. See also corresponding Supplementary Movies S1–S3 and duplicate experiments (Movies S1b–S3b).

vesicle-like aggregates, which can be followed in real time (Fig. 4e–h; Supplementary Movie S2). In another experiment, tri-component nanotube systems were formed comprising switchable amphiphile **1**, the amphiphilic green fluorescent dye 3,3'-dioctyldecyloxycarbocyanine perchlorate (DiO) as well as DOPC (1:DOPC:DiO, 2:1:0.05). This led to the incorporation of DiO in the tube walls of capped nanotubes, resulting in a dramatic increase in the average nanotube length and in the photostability. Irradiation at 390 nm resulted in slow disassembly involving curling/coiling of the nanotubes (Fig. 4i–l; Supplementary Movie S3). We suggest that this enhanced stability is either due to photoquenching by DiO or additional structural stability from the incorporation of the dye amphiphile. These results set the stage for the incorporation of other control or recognition elements in the tubular structure. Finally, studies into dye transfer from a DOPC vesicle to the nanotube and vice versa, using DiO or the red fluorescent analogue DiD, show that transfer of a fluorescent molecule from the bilayer of each of the partners in this hybrid system following fusion is indeed possible (see Supplementary Information, Supplementary Fig. S6). This demonstrates the potential of this arrangement as a controlled release and delivery system, and further investigations in this regard are currently under way.

In conclusion, reversible vesicle removal and light-induced disassembly processes of the vesicle-capped nanotube system shown here

demonstrate how the chemical composition and presence of a responsive function in a constituent building block can be used to trigger and control major changes in the architecture of a complex self-assembled multicomponent nano-object.

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Author contributions

B.L.F. conceived the research. B.L.F., A.C.C., J.M.B., W.R.B. and B.M. designed the experiments. Synthesis of the amphiphile was carried out by B.M., D.J.v.D. and J.C. Solution photochemical studies, switching studies and tube generation were carried out by A.C.C. and B.M. Cryo-TEM was carried out by M.C.A.S. Molecular models were generated by G.C. Confocal microscope and epifluorescence studies were carried out by J.M.B. and J.T.M. A.C.C., J.M.B., W.R.B. and B.L.F. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper at www.nature.com/naturenanotechnology. Reprints and permission information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to B.L.F.