

# The Influence of Side-Chain Halogenation on the Self-Assembly and Hydrogelation of Fmoc-Phenylalanine Derivatives

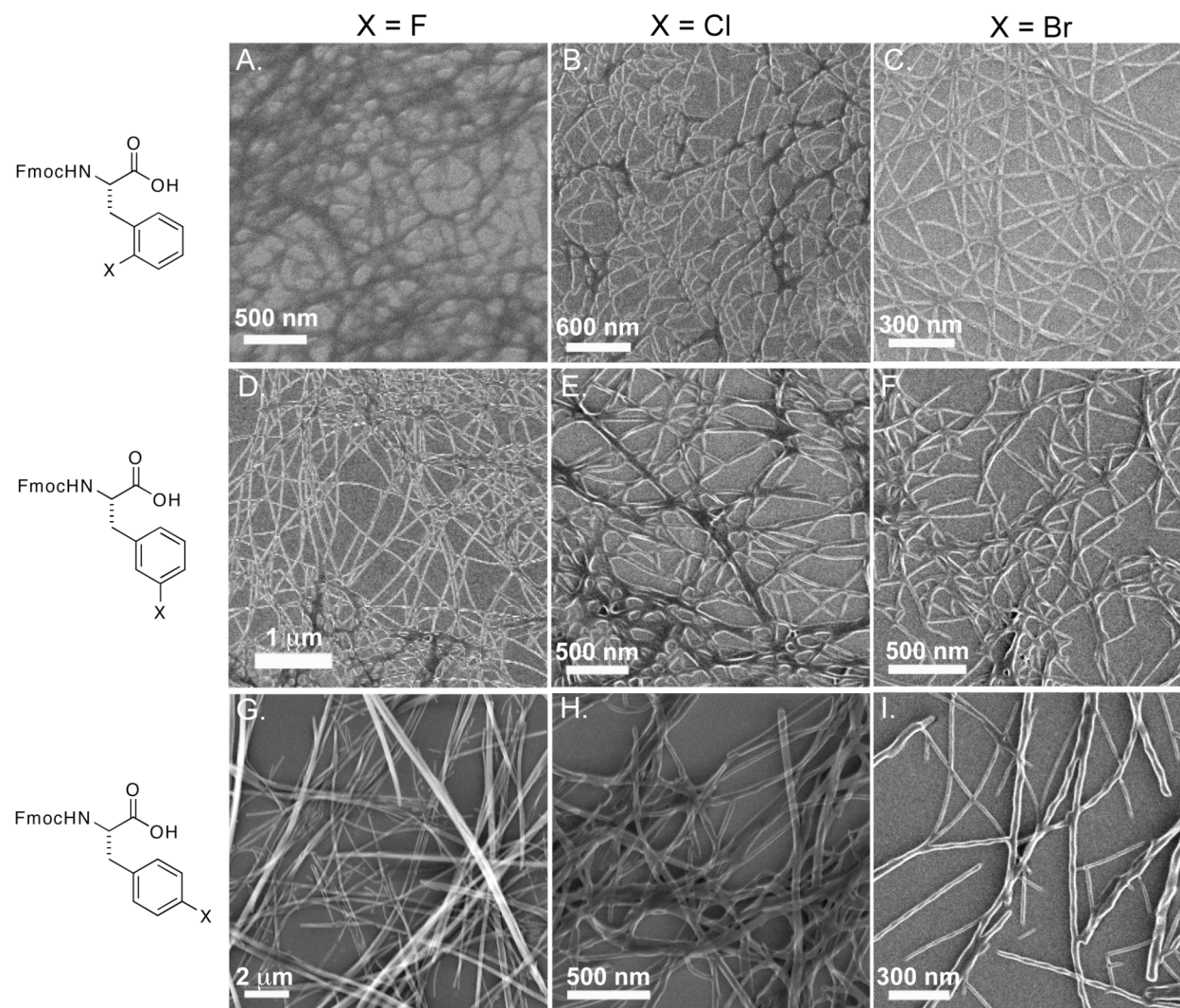
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## ELECTRONIC SUPPORTING INFORMATION

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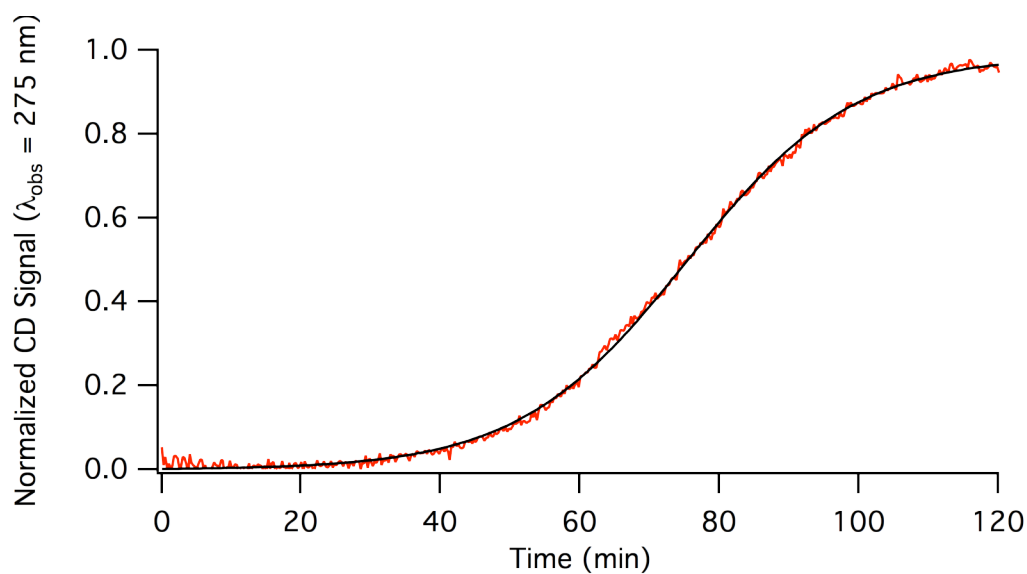
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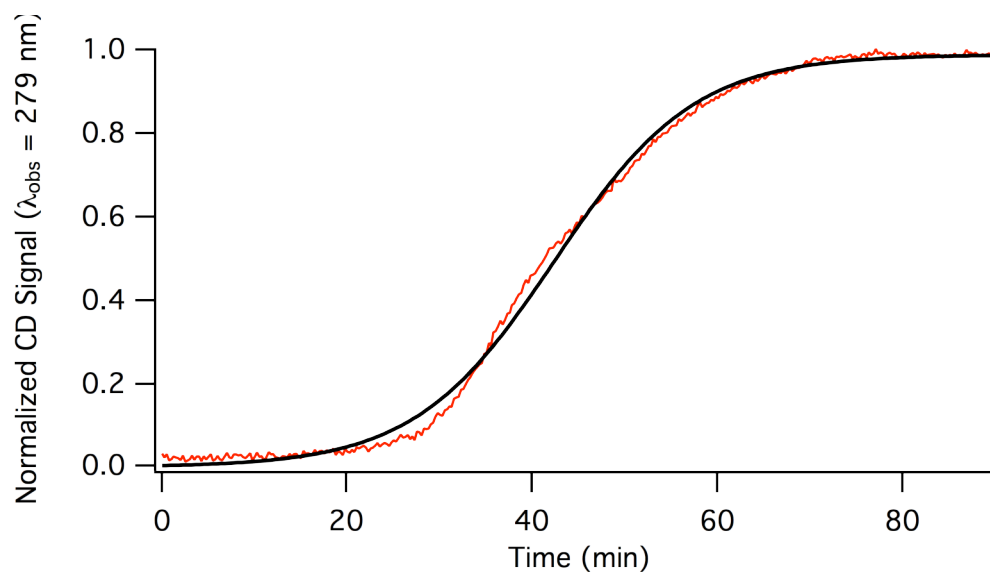
**Figure S1.** SEM images of Fmoc-n-X-Phe amino acids after a 3 day maturation period. A) Fmoc-2-F-Phe; B) Fmoc-2-Cl-Phe; C) Fmoc-2-Br-Phe; D) Fmoc-3-F-Phe; E) Fmoc-3-Cl-Phe; F) Fmoc-3-Br-Phe; G) Fmoc-4-F-Phe; H) Fmoc-4-Cl-Phe; I) Fmoc-4-Br-Phe.

**Table S1.** Tabulation of CD absorptions for each Fmoc-n-X-Phe derived hydrogel (min = minimum, max = maximum).

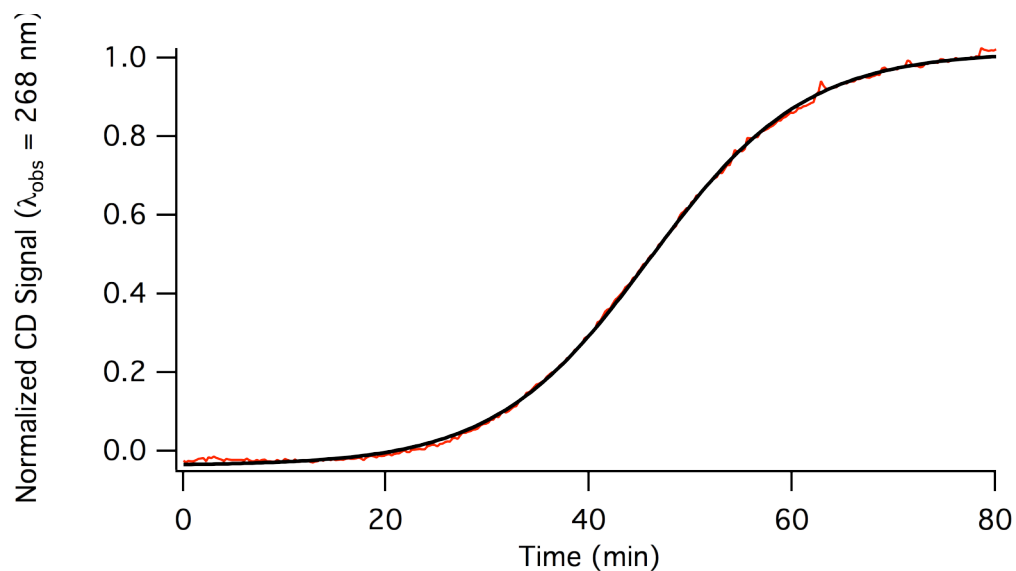
| Amino acid    | Major absorptions (nm)                                |
|---------------|-------------------------------------------------------|
| Fmoc-2-F-Phe  | 200 (min), 224 (max), 275 (max), 293 (max), 307 (max) |
| Fmoc-2-Cl-Phe | 207 (min), 225 (max), 278 (max), 296 (max), 307 (max) |
| Fmoc-2-Br-Phe | 211 (min), 268 (min), 294 (min), 307 (min)            |
| Fmoc-3-F-Phe  | 201 (min), 220 (max), 274 (max), 295 (max), 307 (max) |
| Fmoc-3-Cl-Phe | 207 (min), 226 (max), 276 (max), 295 (max), 307 (max) |
| Fmoc-3-Br-Phe | 210 (min), 228 (max), 279 (max), 296 (max), 309 (max) |
| Fmoc-4-F-Phe  | 229 (min), 289 (min), 298 (min), 310 (min)            |
| Fmoc-4-Cl-Phe | 209 (min), 231 (min), 279 (min), 296 (min), 309 (min) |
| Fmoc-4-Br-Phe | 213 (min), 232 (max), 284 (max), 296 (max), 309 (max) |



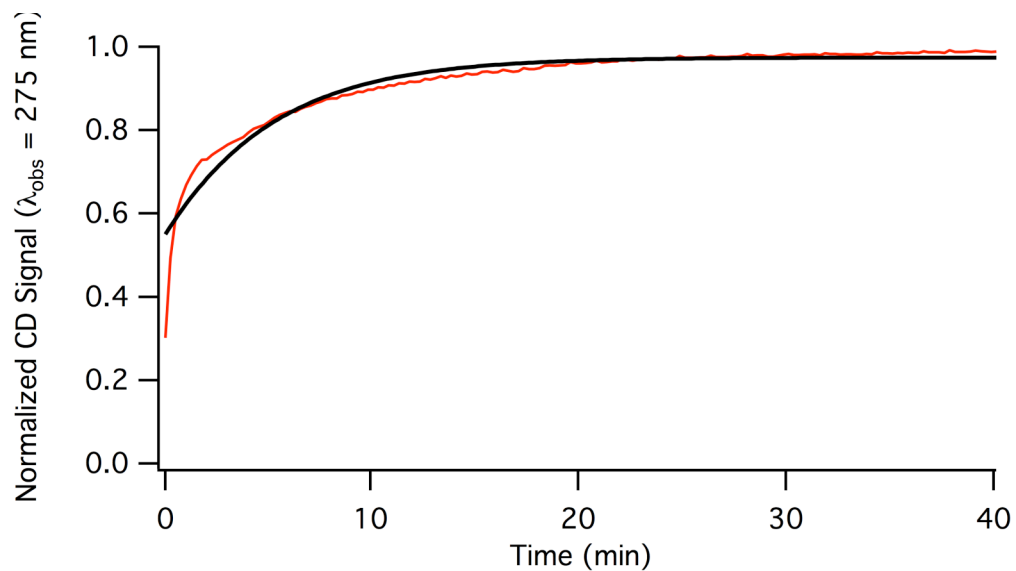
**Figure S2.** Representative empirical curve fit for Fmoc-2-F-Phe self-assembly kinetics ( $t_{1/2} = 75 \pm 5 \text{ min}$ ,  $k = 0.08 \pm 0.02 \text{ min}^{-1}$ ).



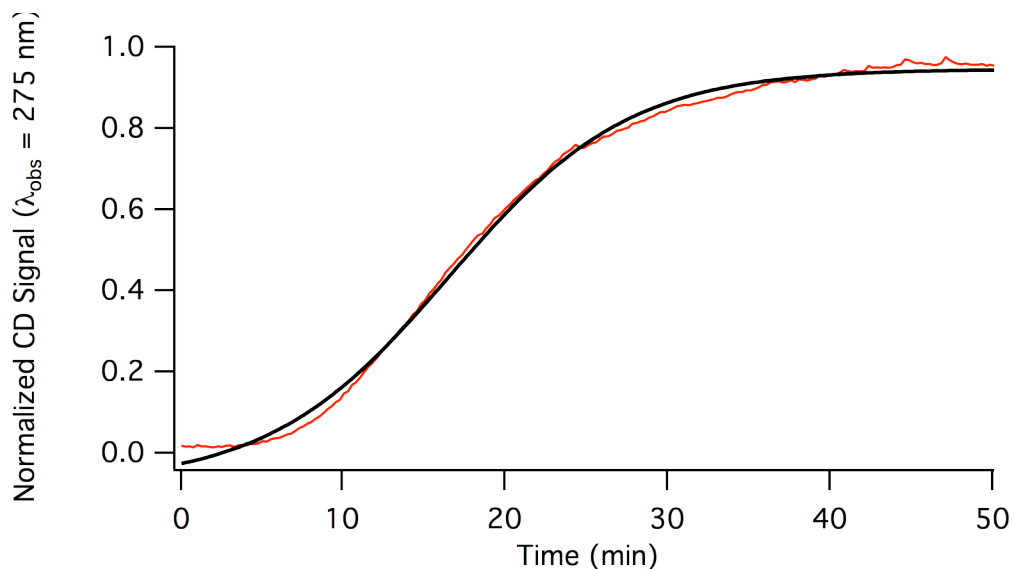
**Figure S3.** Representative empirical curve fit for Fmoc-2-Cl-Phe self-assembly kinetics ( $t_{1/2} = 41 \pm 4 \text{ min}$ ,  $k = 0.2 \pm 0.1 \text{ min}^{-1}$ ).



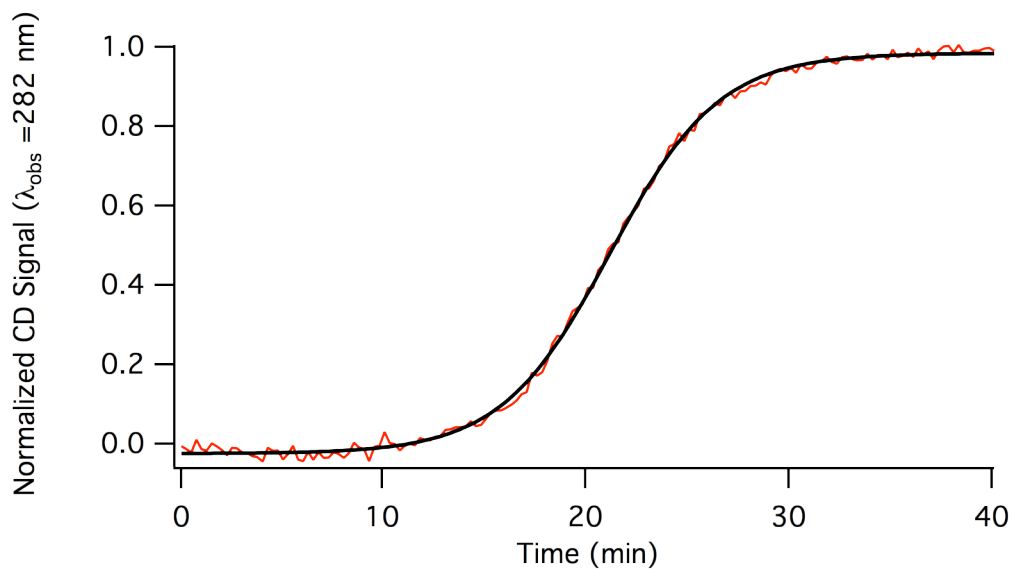
**Figure S4.** Representative empirical curve fit for Fmoc-2-Br-Phe self-assembly kinetics ( $t_{1/2} = 47 \pm 3 \text{ min}$ ,  $k = 0.12 \pm 0.03 \text{ min}^{-1}$ ).



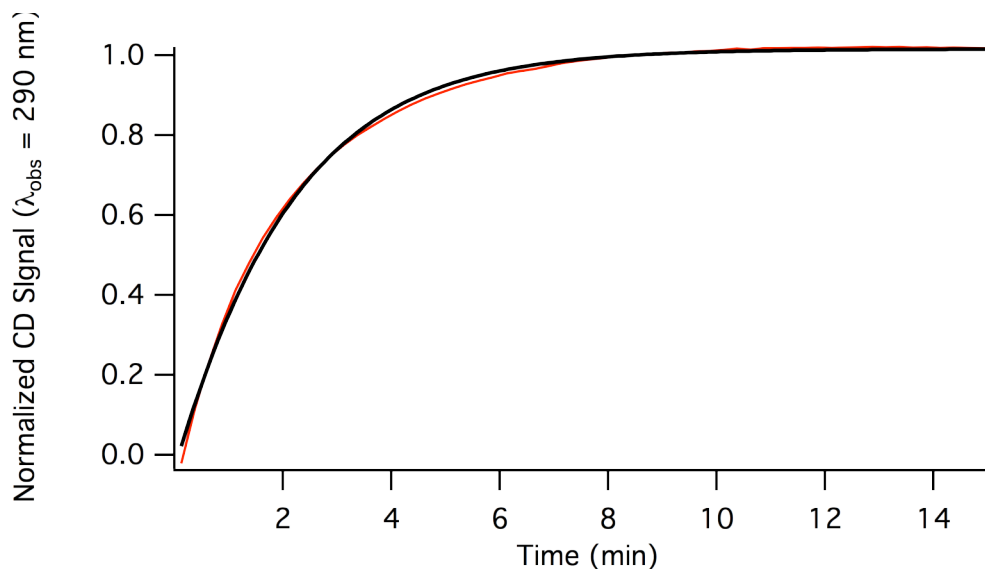
**Figure S5.** Representative empirical curve fit for Fmoc-3-F-Phe self-assembly kinetics (reliable  $t_{1/2}$  and  $k$  values could not be obtained to the lack of an observable lag phase).



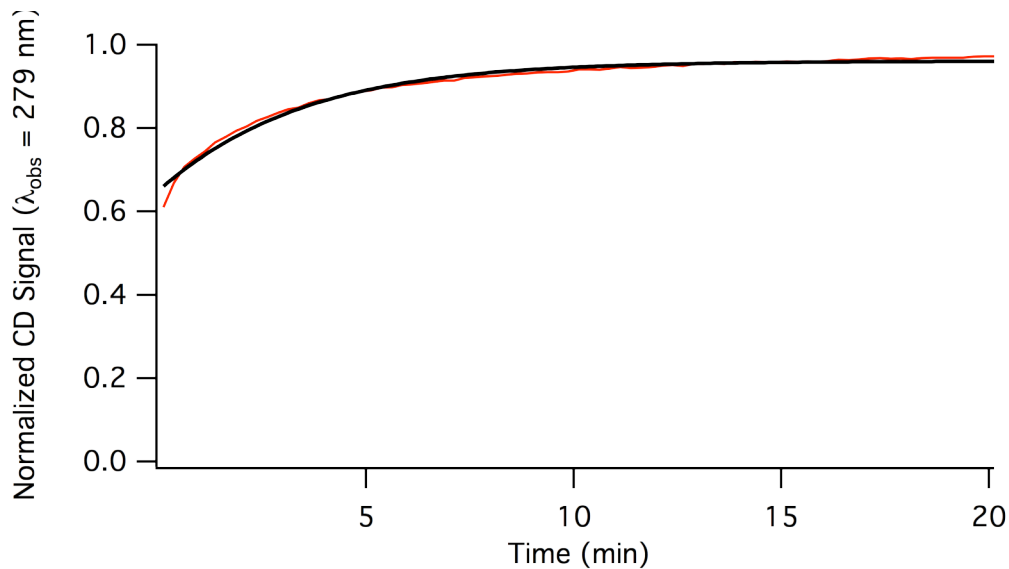
**Figure S6.** Representative empirical curve fit for Fmoc-3-Cl-Phe self-assembly kinetics ( $t_{1/2} = 18 \pm 2 \text{ min}$ ,  $k = 0.23 \pm 0.03 \text{ min}^{-1}$ ).



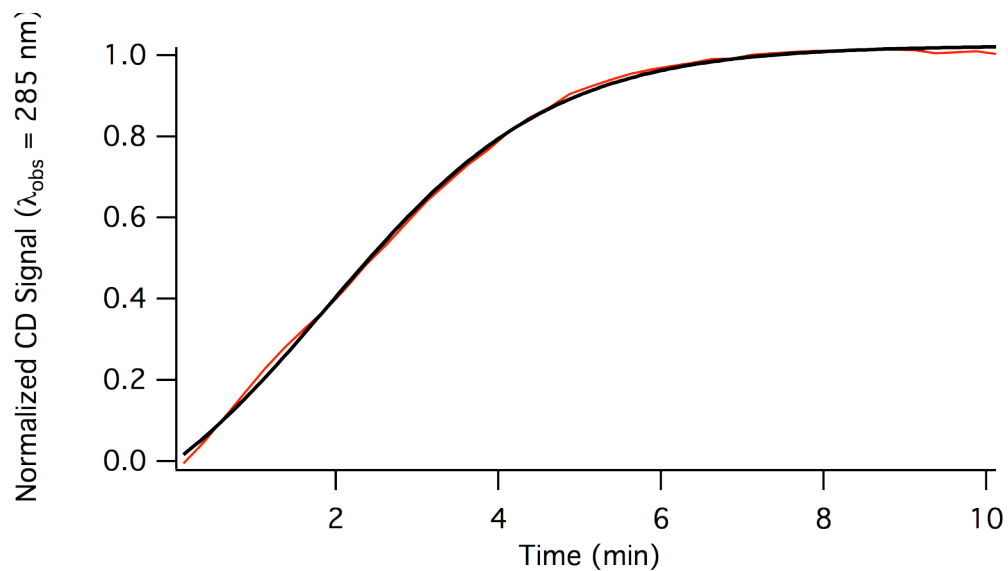
**Figure S7.** Representative empirical curve fit for Fmoc-3-Br-Phe self-assembly kinetics ( $t_{1/2} = 21 \pm 1 \text{ min}$ ,  $k = 0.6 \pm 0.3 \text{ min}^{-1}$ ).



**Figure S8.** Representative empirical curve fit for Fmoc-4-F-Phe self-assembly kinetics (reliable  $t_{1/2}$  and  $k$  values could not be obtained to the lack of an observable lag phase).

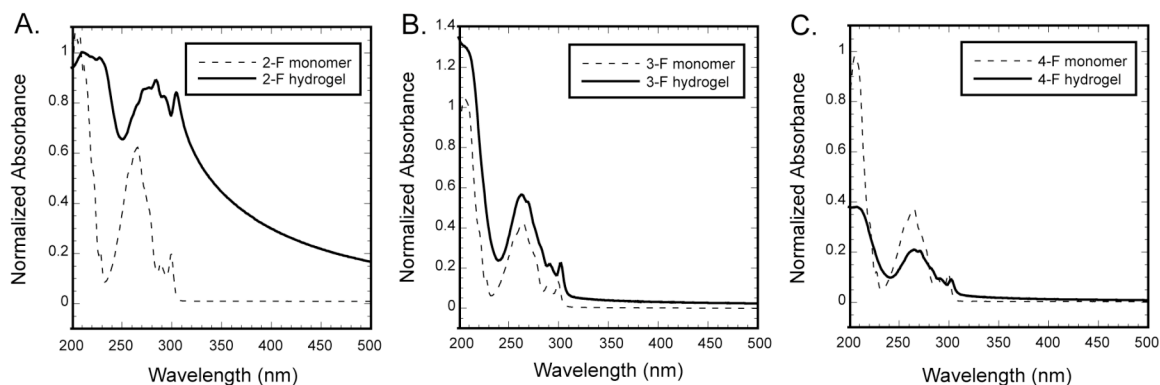


**Figure S9.** Representative empirical curve fit for Fmoc-4-Cl-Phe self-assembly kinetics (reliable  $t_{1/2}$  and  $k$  values could not be obtained to the lack of an observable lag phase).

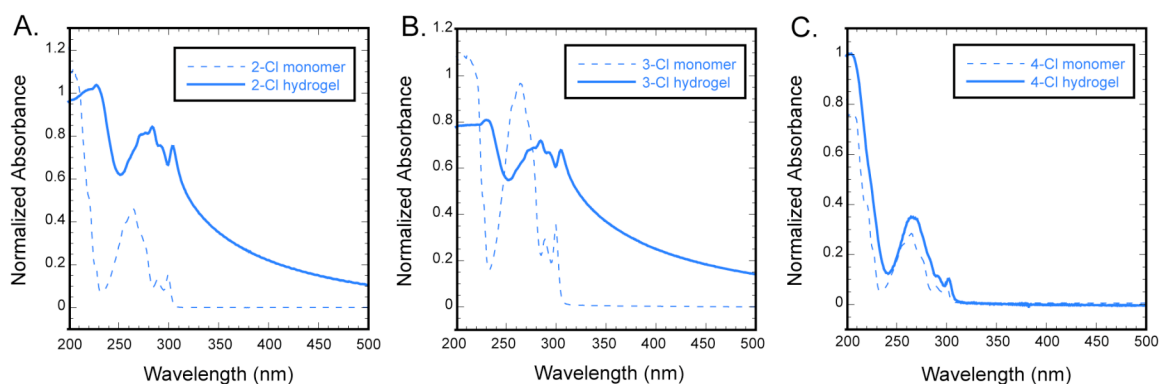


**Figure S10.** Representative empirical curve fit for Fmoc-4-Br-Phe self-assembly kinetics (reliable  $t_{1/2}$  and  $k$  values could not be obtained to the lack of an observable lag phase).

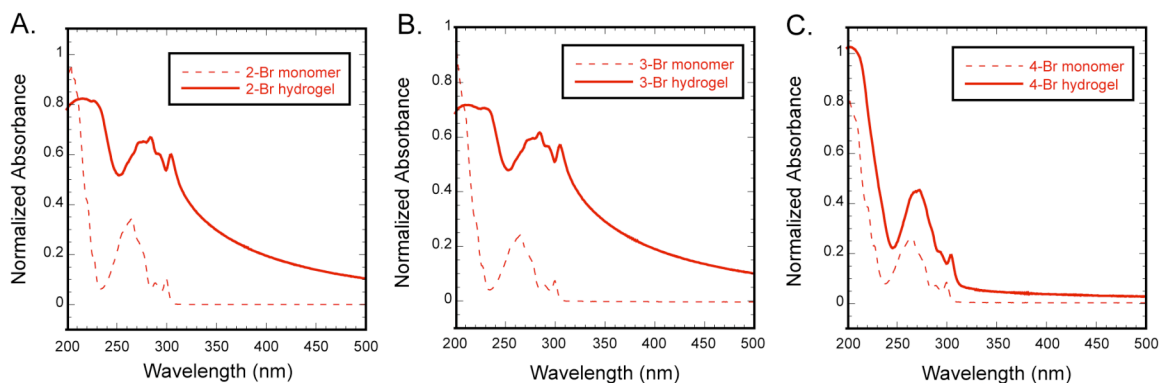




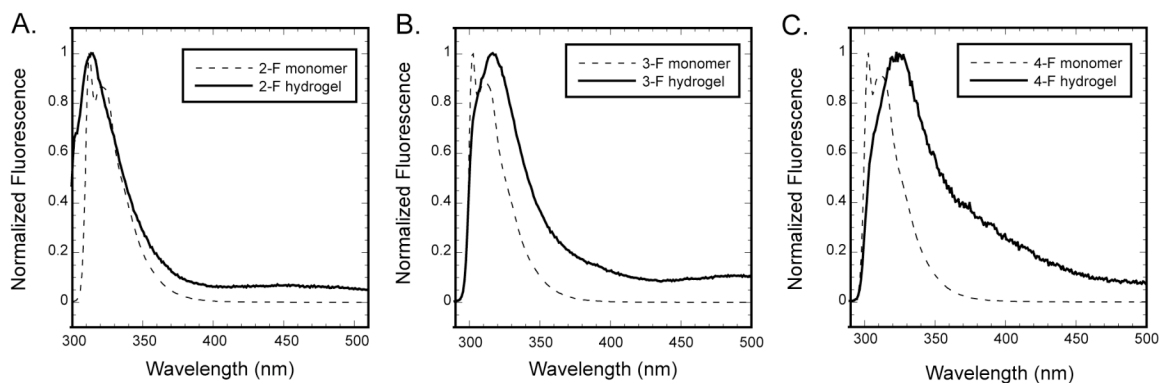
**Figure S11.** Normalized UV-Vis absorbance of monomeric Fmoc-n-F-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-n-F-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-F-Phe; B) Fmoc-3-F-Phe; C) Fmoc-3-Cl-Phe.



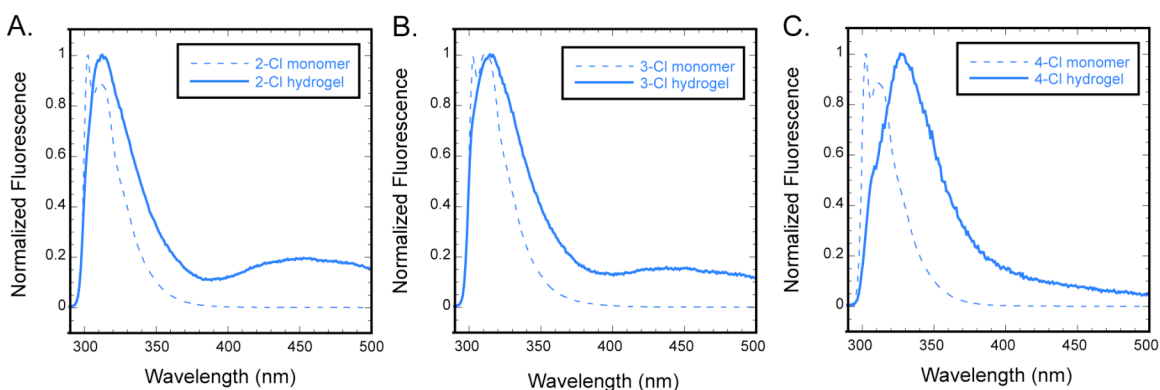
**Figure S12.** Normalized UV-Vis absorbance of monomeric Fmoc-n-Cl-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-n-Cl-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-Cl-Phe; B) Fmoc-3-Cl-Phe; C) Fmoc-4-Cl-Phe.



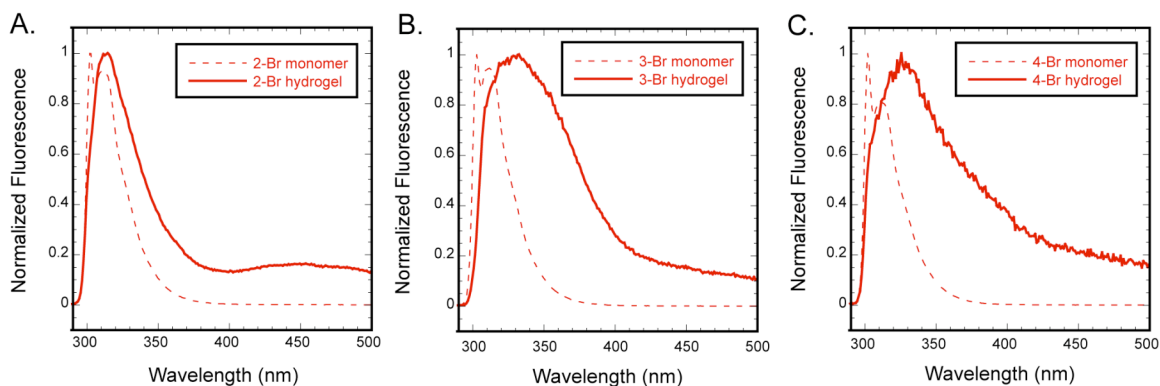
**Figure S13.** Normalized UV-Vis absorbance of monomeric Fmoc-n-Br-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-n-Br-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-Br-Phe; B) Fmoc-3-Br-Phe; C) Fmoc-4-Br-Phe.



**Figure S14.** Normalized fluorescence emission spectra of monomeric Fmoc-n-Br-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-X-Br-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-Br-Phe; B) Fmoc-3-Br-Phe; C) Fmoc-4-Br-Phe.



**Figure S15.** Normalized fluorescence emission spectra of monomeric Fmoc-n-Br-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-n-Br-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-Br-Phe; B) Fmoc-3-Br-Phe; C) Fmoc-4-Br-Phe.



**Figure S16.** Normalized fluorescence emission spectra of monomeric Fmoc-n-Br-Phe derivatives (4.94 mM in MeOH) and assembled Fmoc-n-Br-Phe derivatives (4.94 mM in 2% MeOH/H<sub>2</sub>O). A) Fmoc-2-Br-Phe; B) Fmoc-3-Br-Phe; C) Fmoc-4-Br-Phe.