

Supporting Information

Assembly of metallacages into Soft Suprastructures with Dimensions of up to Microns and the Formation of Composite Materials

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Additional NMR, UV-vis, and fluorescence spectra data, scanning electron microscope, transmission electron microscopy, and fluorescence microscope images were provided in the Supporting Information.

Supporting Information

1.1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of cage 1	S4
1.2 ^1H NMR spectrum of cage 1	S4
1.3 ESI -TOF-MS spectrum of cage 1	S5
1.4 UV-vis spectrum of cage 1 (10 μM) in DCM	S5
1.5 UV-vis spectrum of cage 1 (10 μM) in EA	S6
1.6 UV-vis spectrum of Cage 1 (10 μM) in DCM/EA mixture with 80% EA	S6
1.7 Fluorescence spectrum of cage 1 (10 μM) in DCM.	S7
1.8 Fluorescence spectrum of cage 1 (10 μM) in EA.	S7
1.9 Fluorescence spectrum of Cage 1 (10 μM) in DCM/EA mixture with 80% EA	S8
1.10 Corresponding histograms of microflowers formed in 80 % EA	S8
1.11 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of cage 1 -based microflowers	S9
1.12 Fluorescence microscopy images of microflowers formed in 80 % EA	S9
1.13 ^1H NMR spectrum of cage 1 -based microflowers	S10
1.14 ESI -TOF-MS spectrum of cage 1 formed in 80 % EA	S10
1.15 Simulated structure of the cage 1	S11
1.16 SEM images of (a) nanostructures formed in 90% EA	S11
1.17 XRD profile	S12
1.18 Fluorescence spectra of cage 1	S13
1.19 UV-vis spectra of cage 1	S13
1.20 NMR spectra of cage 1 in DCM/EA mixtures	S14
1.21 Assemblies obtained at different times	S15
1.22 Elemental mapping analysis of microneedles/microflowers	S15
1.23 Microneedles/microflowers obtained at different temperature	S15
1.24 Chemical structure of lysine-modified perylene	S16
1.25 Histograms of the size distribution of microflowers formed in 80% EA	S16
1.26 Optical and polarized images of needle-based flowers formed by the coassembly of cage 1 and perylene	S16
1.27 SAXS profile of needle-based flowers formed by the coassembly of cage 1 and perylene	S17

1.28 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra microflowers redispersed in DCM	S17
1.29 ^1H -NMR of cage 1 , perylene, and the mixture of cage 1 and perylene	S18
1.30 Fluorescence microscopy images of the chlorophyll-a containing assemblies	S18
1.31 ^1H -NMR of cage 1 , chlorophyll-a, and the mixture of cage 1 and chlorophyll-a	S19
1.32 Fluorescence microscopy images of the chlorophyll-a containing assemblies	S19
1.33 ^1H -NMR of cage 1 , Vitamin B ₁₂ , and the mixture of cage 1 and Vitamin B ₁₂	S20

1.1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (300 MHz, CD_2Cl_2) recorded for cage **1**.

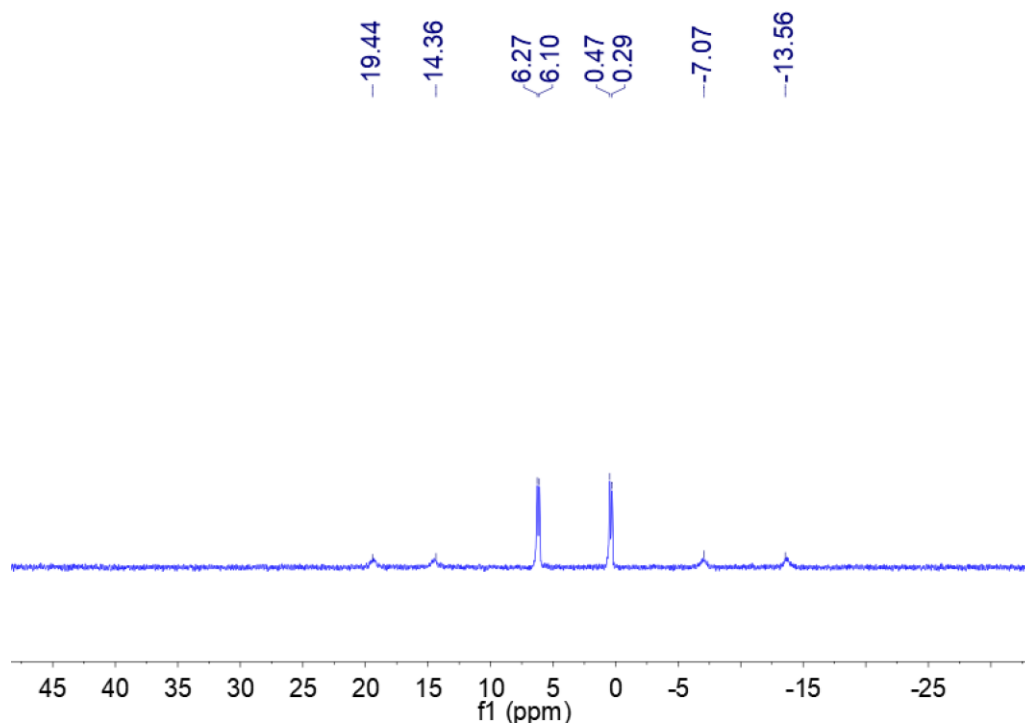


Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2) recorded for cage **1**.

1.2 ^1H NMR spectrum of cage **1**.

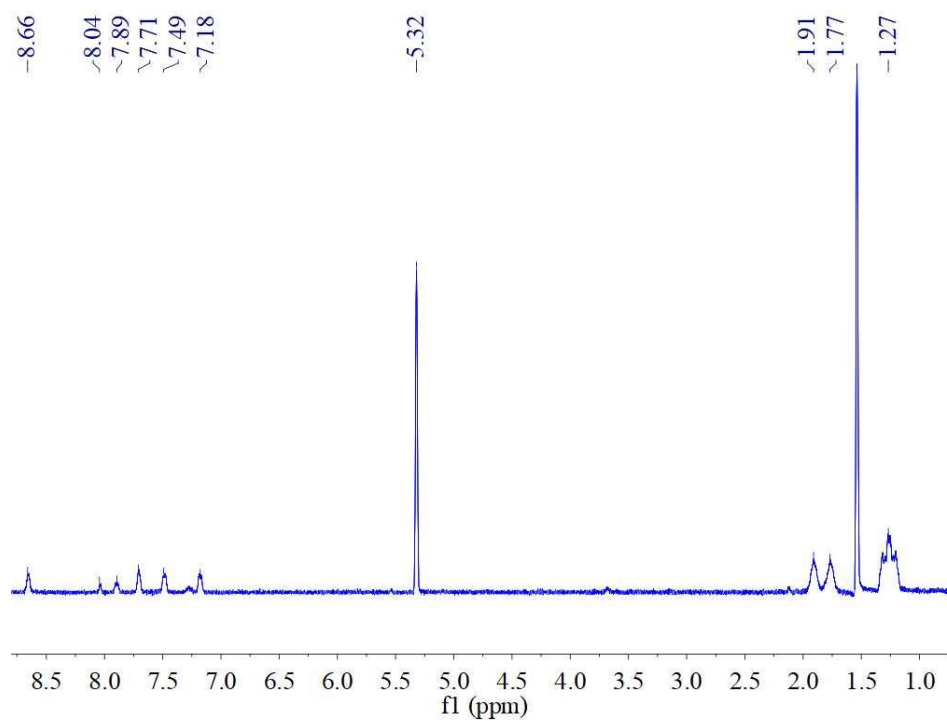


Figure S2. ^1H NMR spectrum (400 MHz, CD_2Cl_2) recorded for cage **1**.

1.3 ESI -TOF-MS spectrum of cage 1.

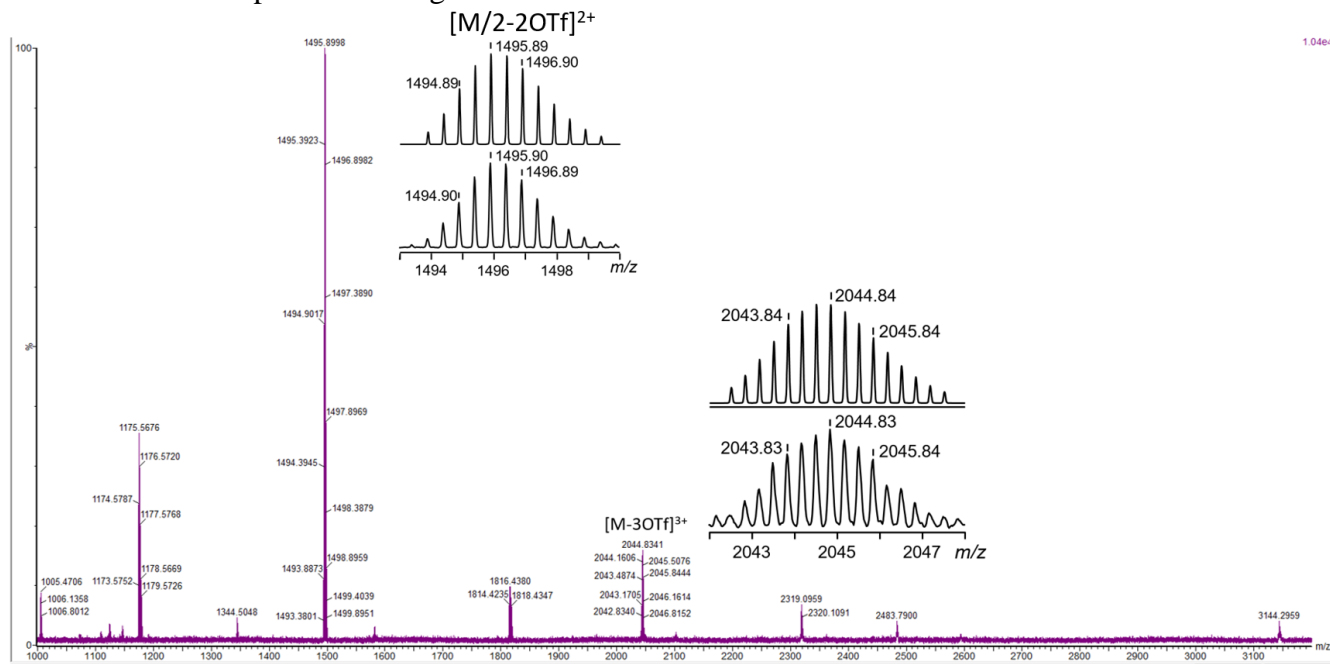


Figure S3. ESI -TOF-MS spectrum of cage 1.

1.4 UV-vis spectrum of cage 1 (10 μ M) in DCM.

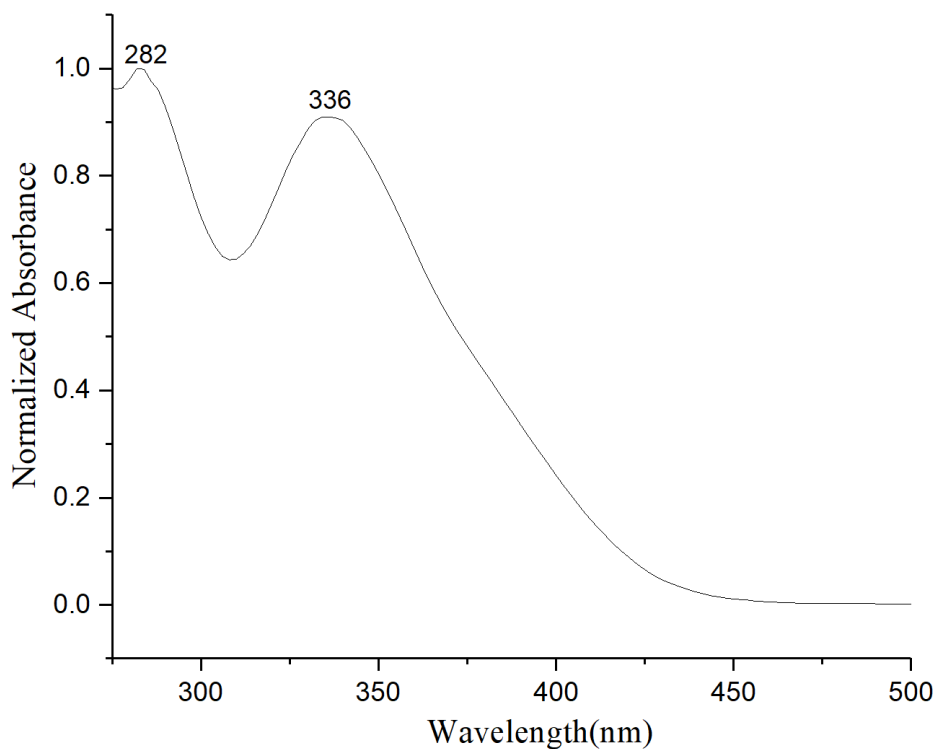


Figure S4. UV-vis spectrum of cage 1 (10 μ M) in DCM.

1.5 UV-vis spectrum of cage 1 (10 μ M) in EA

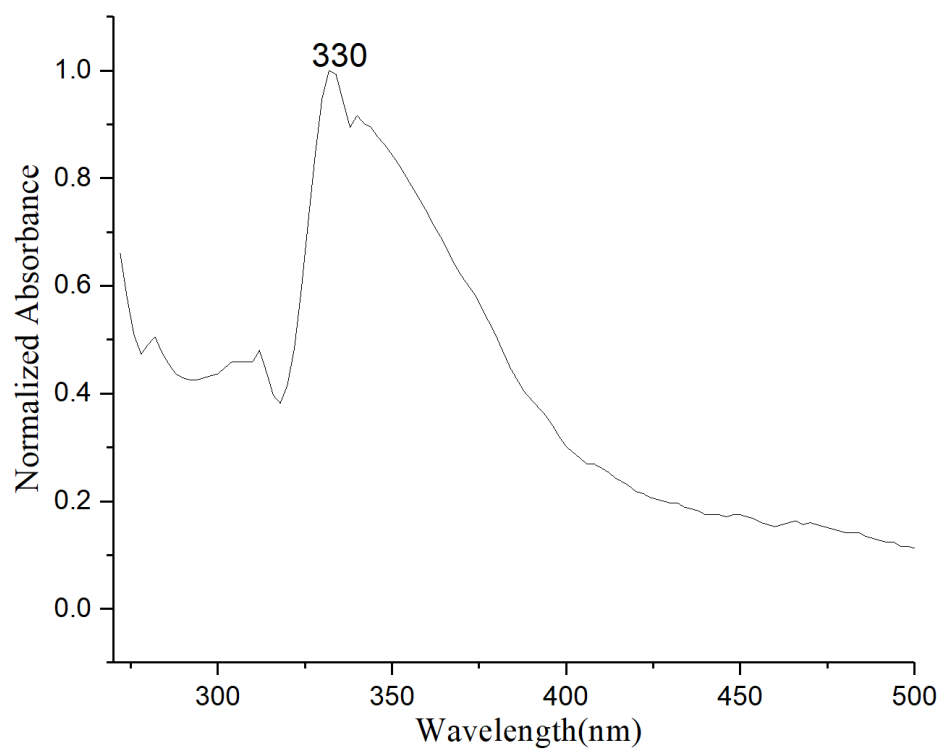


Figure S5. UV-vis spectrum of cage 1 (10 μ M) in EA.

1.6 UV-vis spectrum of cage 1 in DCM/EA mixture with 80% EA

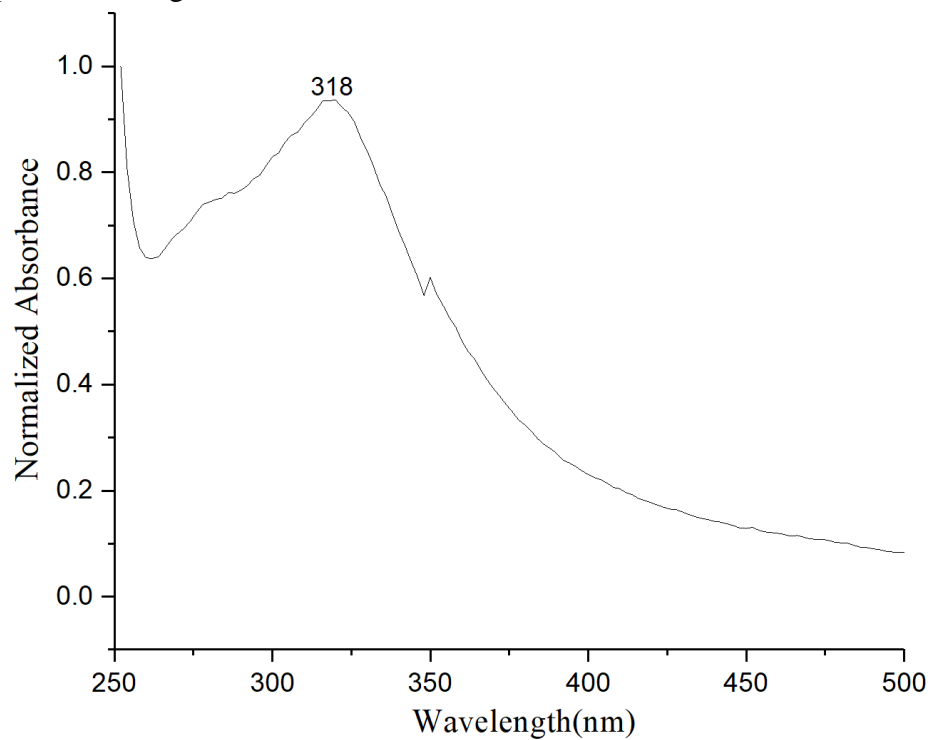


Figure S6. UV-vis spectrum of cage 1 (10 μ M) in DCM/EA mixture with 80% EA.

1.7 Fluorescence spectrum of cage 1 in DCM

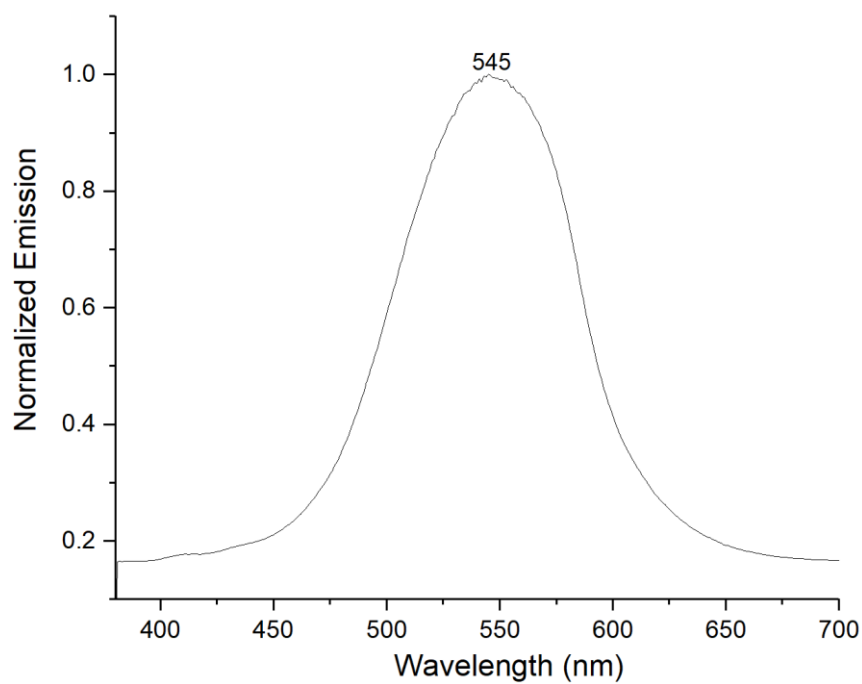


Figure S7. Fluorescence spectrum of cage 1 (10 μ M) in DCM.

1.8 Fluorescence spectrum of cage 1 in EA

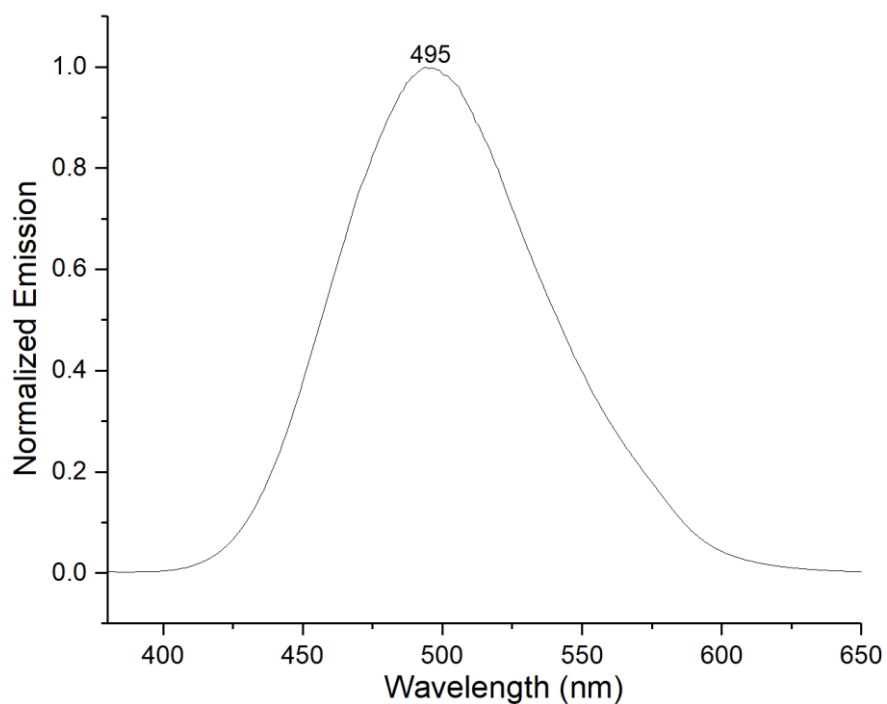


Figure S8. Fluorescence spectrum of cage 1 (10 μ M) in EA.

1.9 Fluorescence spectrum of cage 1 (10 μM) in DCM/EA mixture with 80% EA

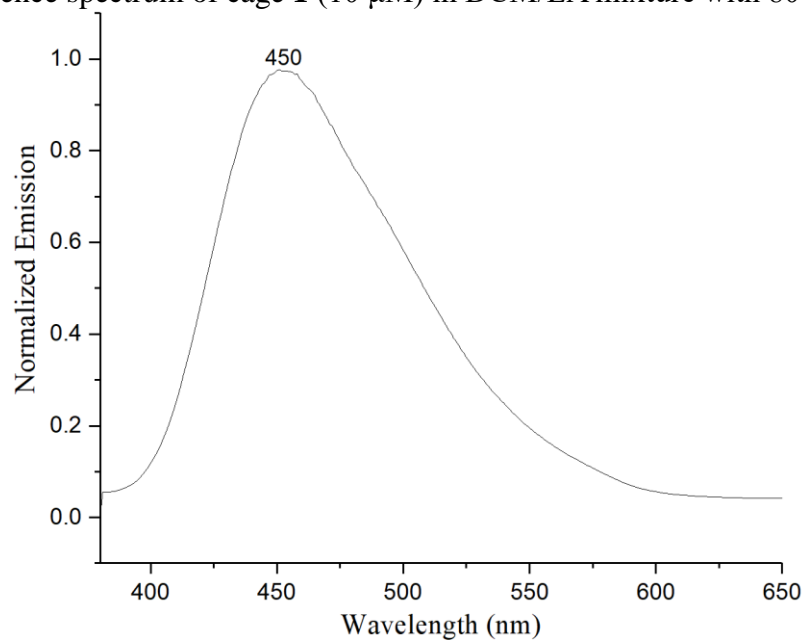


Figure S9. Fluorescence spectrum of cage 1 (10 μM) in DCM/EA mixture with 80% EA.

1.10 Corresponding histograms of microflowers formed in 80 % EA

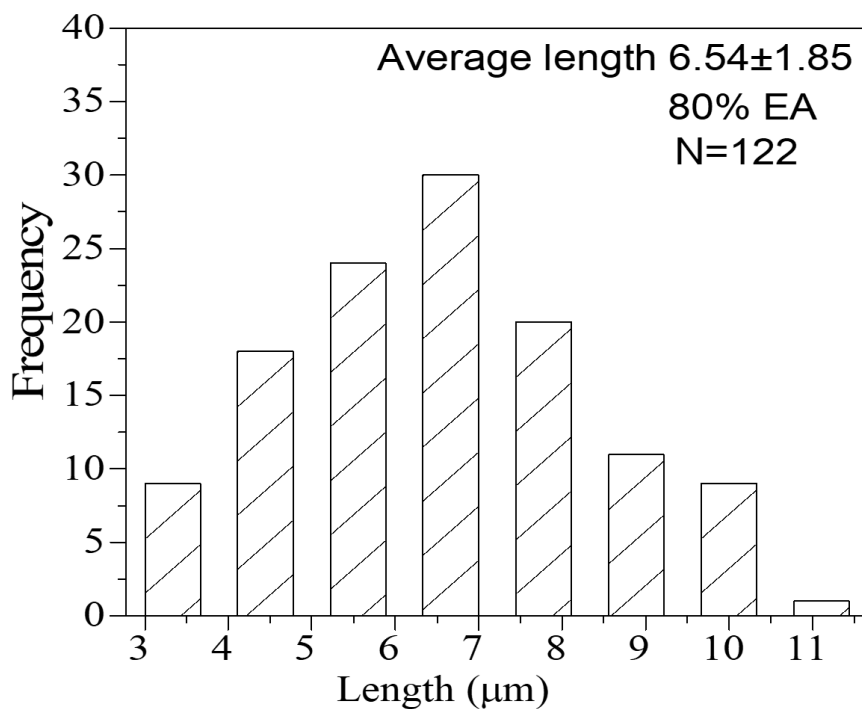


Figure S10. Corresponding histograms of the size distribution of needle-based microflowers (in Figure 1d).

1.11 Fluorescence microscopy images of microflowers formed in 80 % EA

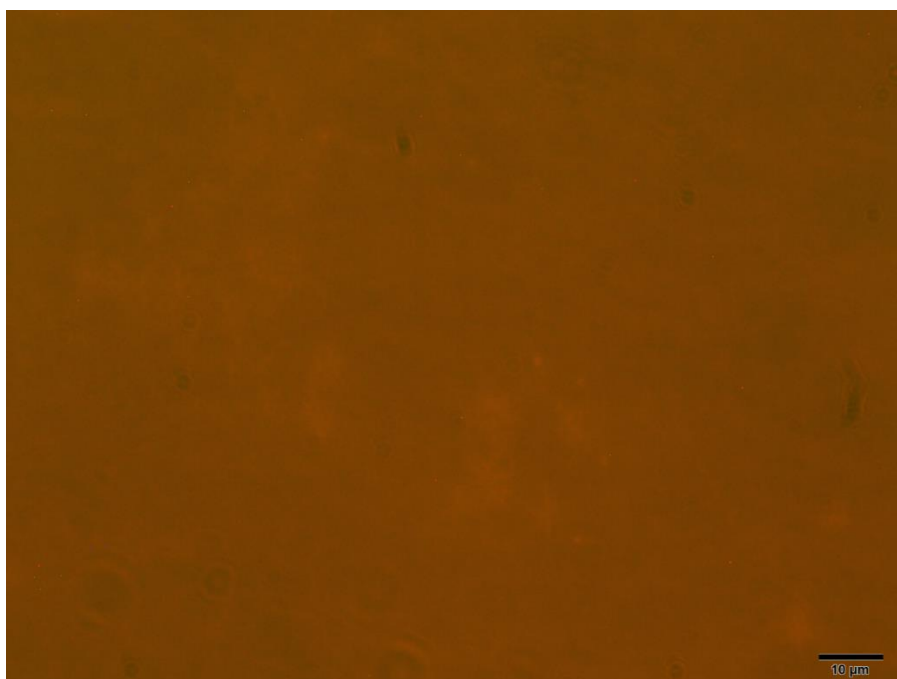


Figure S11. Fluorescence microscopy images of these assemblies (in Figure 1e-f) under green-light excitation.

1.12 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of cage **1**-based microflowers

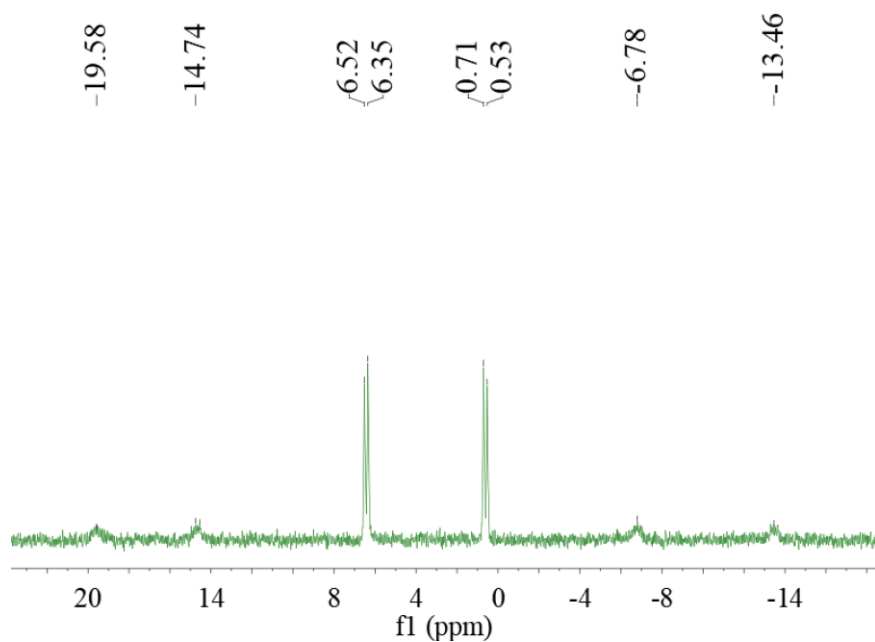


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of cage **1**-based microflowers redispersed in DCM.

1.13 ^1H NMR spectrum of cage **1**-based microflowers

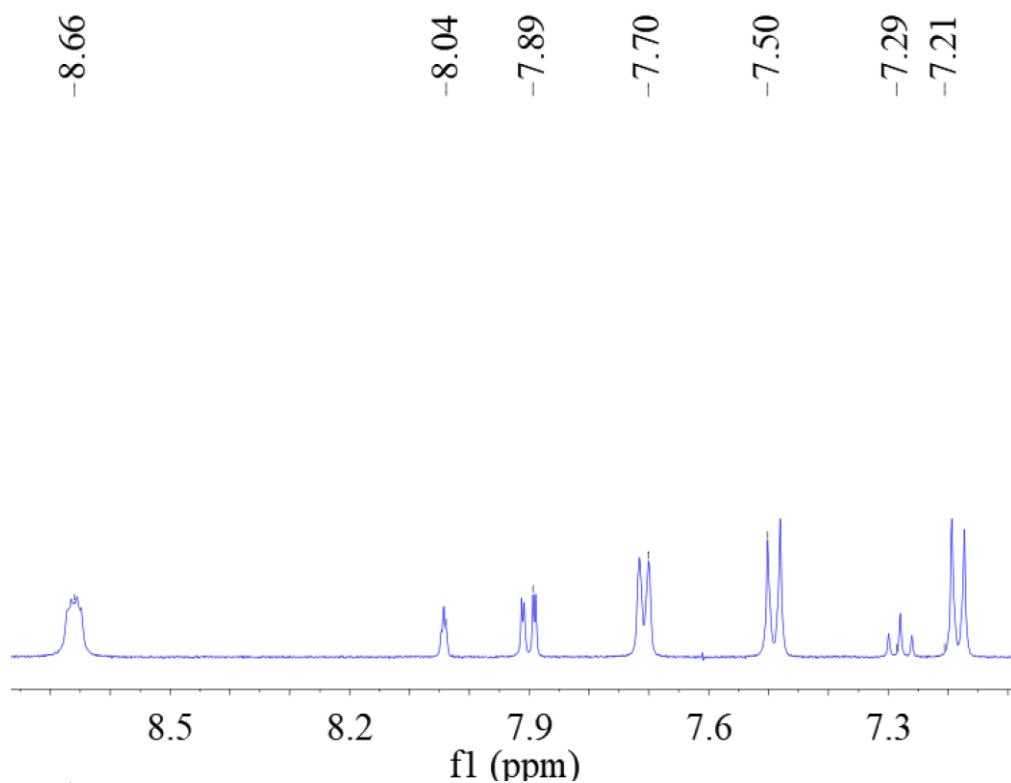


Figure S13. ^1H NMR spectrum of cage **1**-based microflowers redispersed in DCM.

1.14 ESI -TOF-MS spectrum of cage **1** formed in 80 % EA

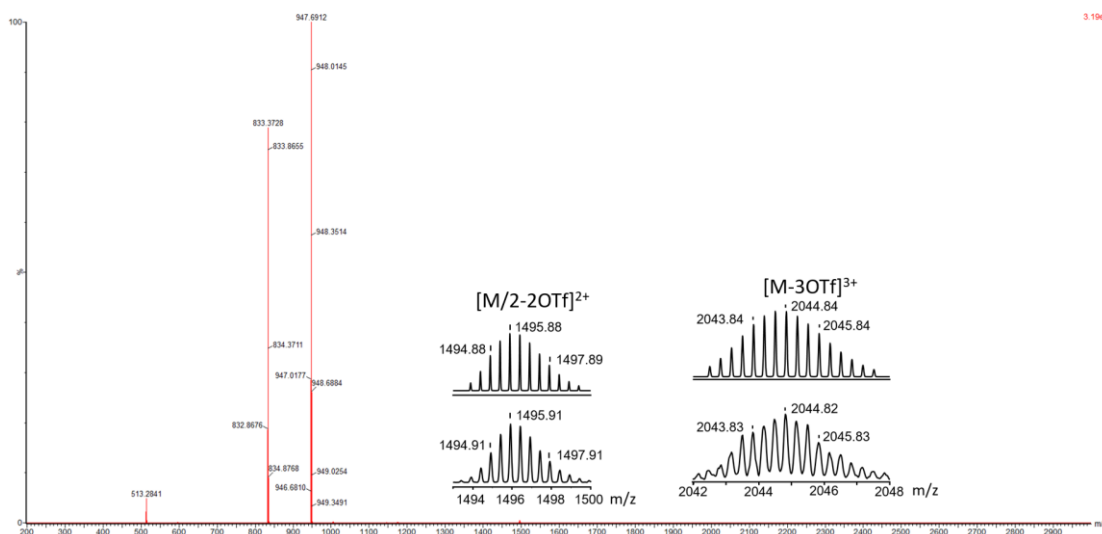


Figure S14. ESI -TOF-MS spectrum of cage **1**.

1.15 Simulated structure of the cage 1

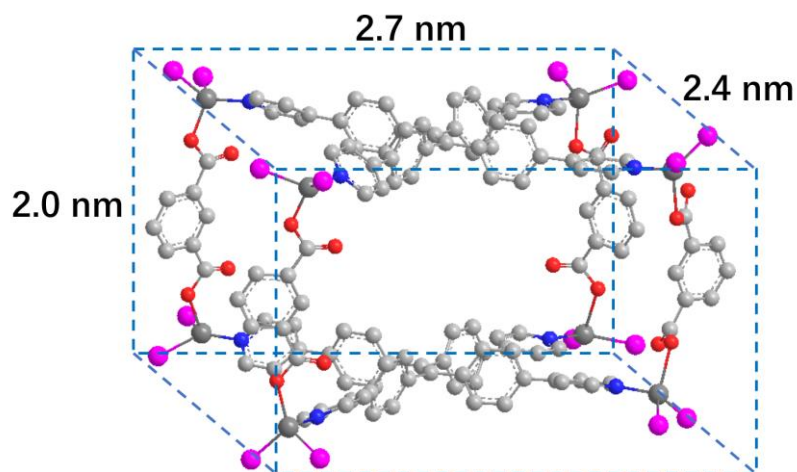


Figure S15. Simulated structure of the cage 1.

1.16 SEM images of nanostructures formed in 90% EA

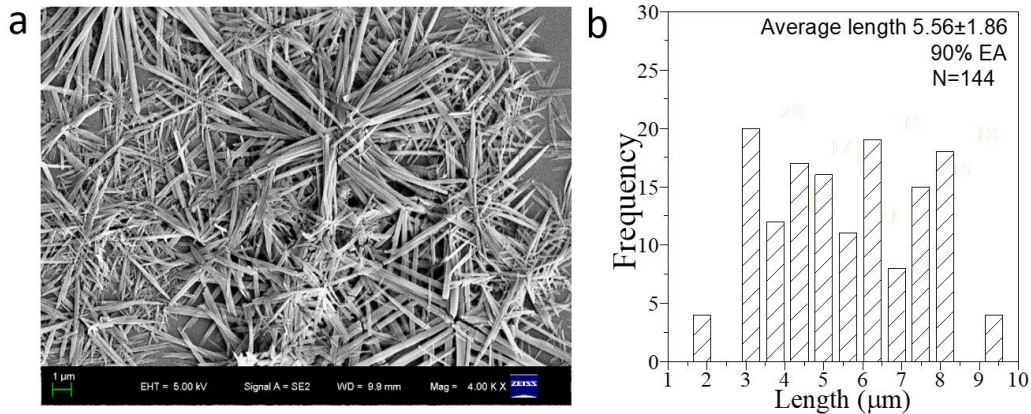


Figure S16. SEM images of (a) nanostructures formed from cage 1 (10 μM) in DCM/EA mixture (fresh prepared) with 90%. (b) Histograms of the size distribution of needle-based microflowers formed from cage M (10 μM) in DCM/EA mixture (fresh prepared) with 90% EA.

1.17 XRD profile

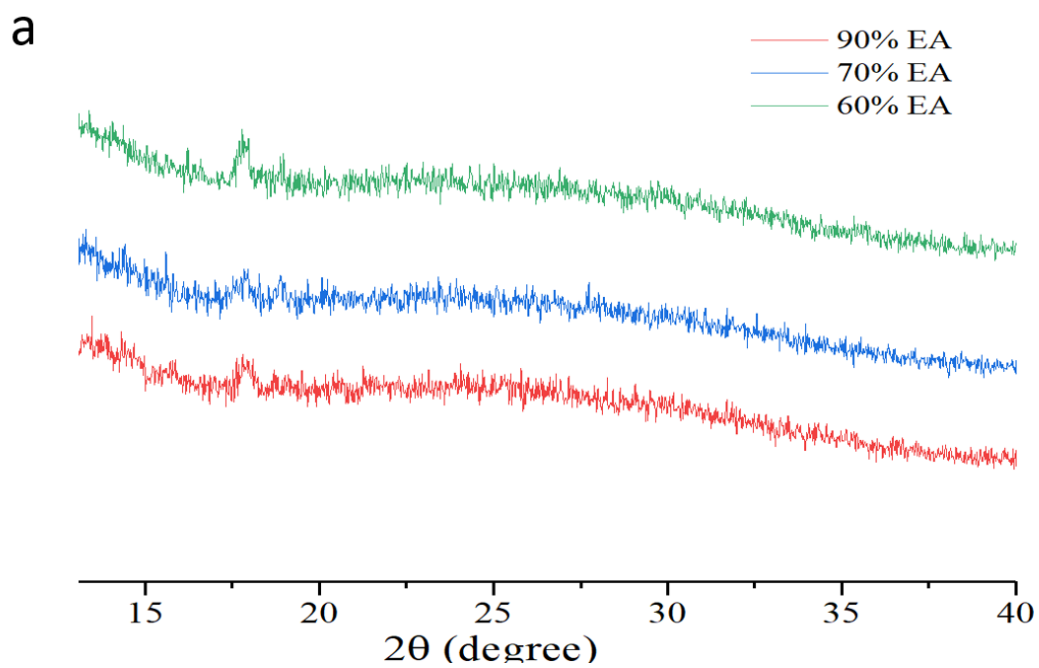


Figure S17. XRD profile of microflowers.

1.18 Fluorescence spectra of cage 1.

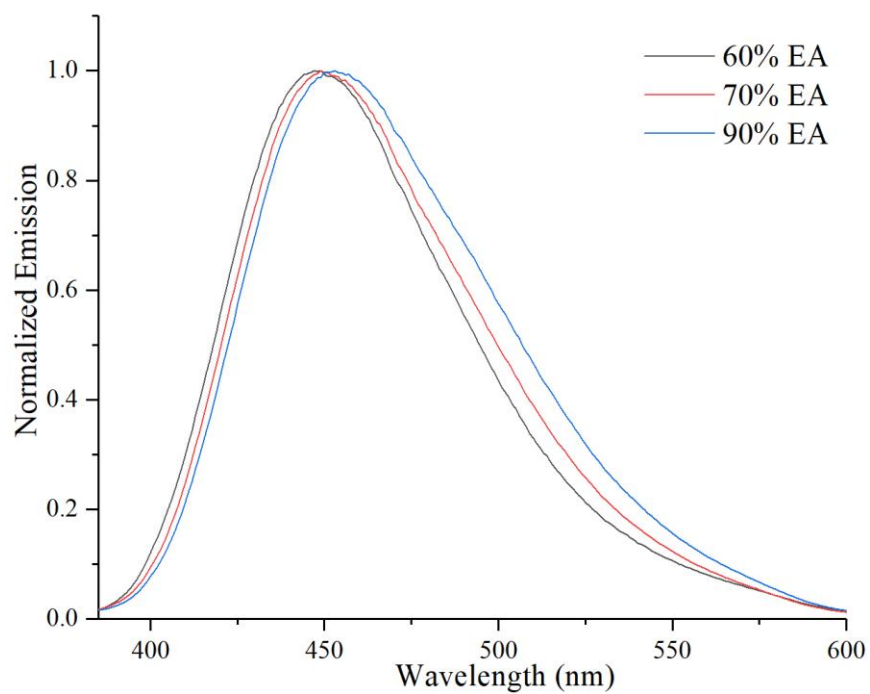


Figure S18. Fluorescence spectra of cage 1 (10 μ M) in DCM/EA mixture.

1.19 UV-vis spectra of cage 1.

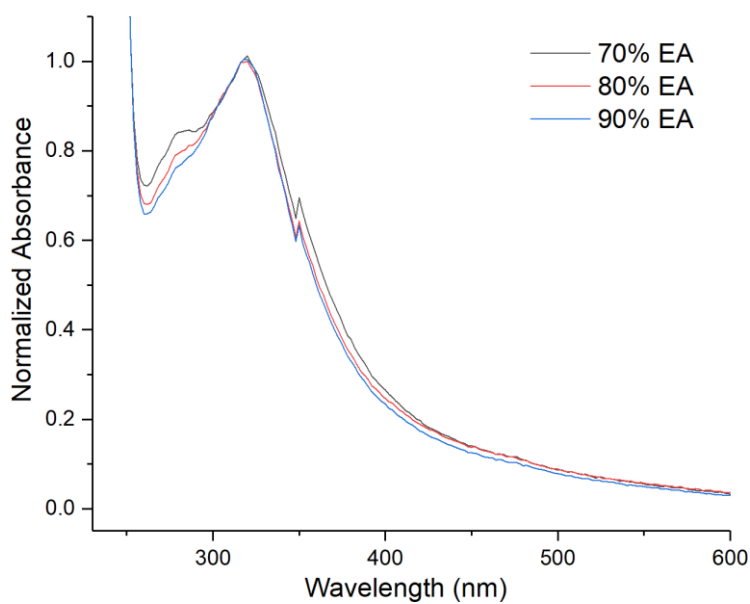


Figure S19. UV-vis spectra of cage 1 (10 μ M) in DCM/EA mixture.

1.20 NMR spectra of cage 1 (100 μ M) in DCM/EA mixtures

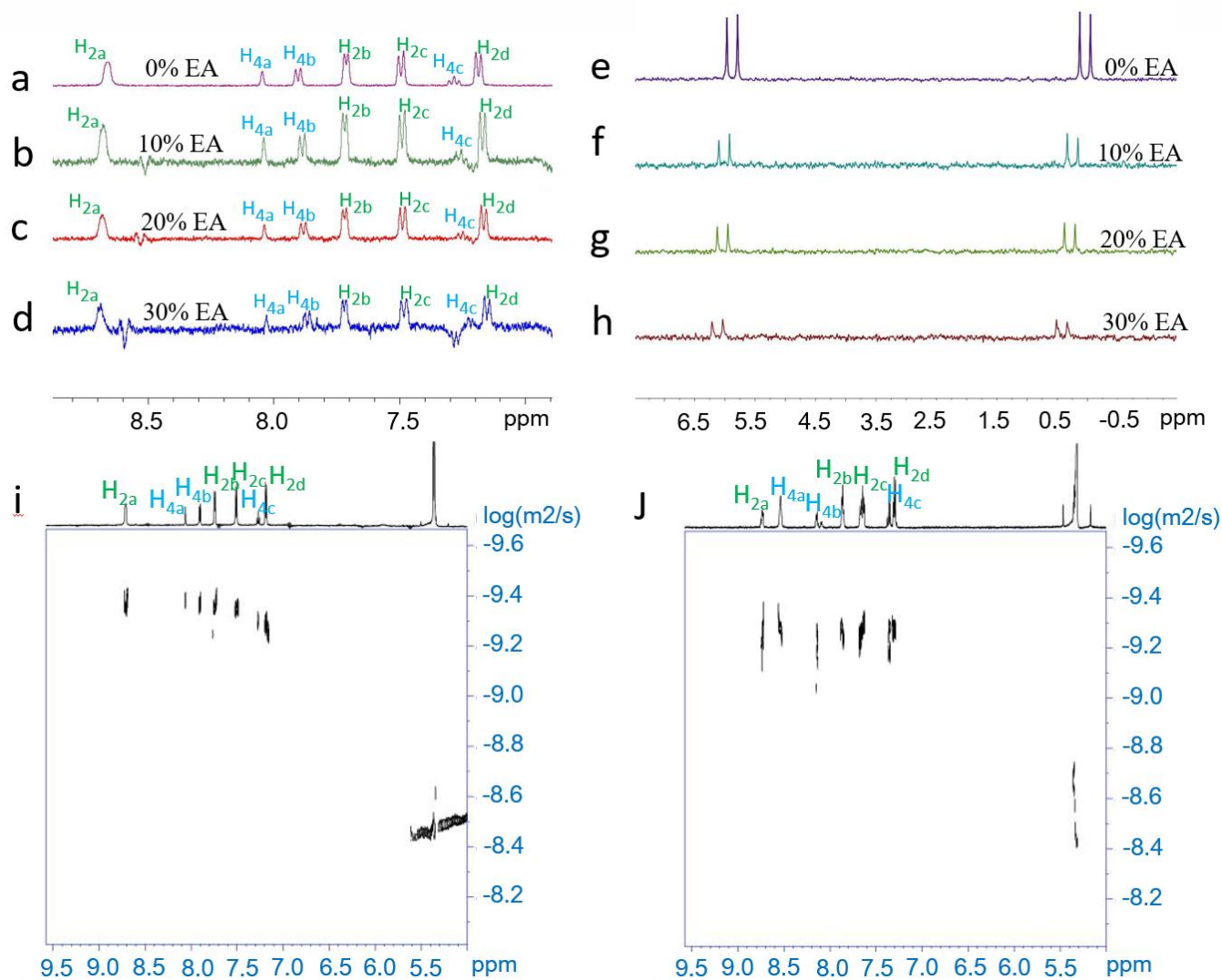


Figure S20. ^1H NMR spectra of cage 1 (100 μM) in DCM/EA mixtures with (b) 0%, (c) 10%, (d) 20%, and (e) 30% EA. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of cage 1 (100 μM) in DCM/EA mixtures with (f) 0%, (g) 10%, (h) 20%, and (i) 30% EA. 2D DOSY NMR spectra (600 MHz) of Cage 1 in (j) DCM/EA mixture with EA content is 10% (100 μM); (k) in pure DCM (100 μM).

1.21 Assemblies obtained at different times

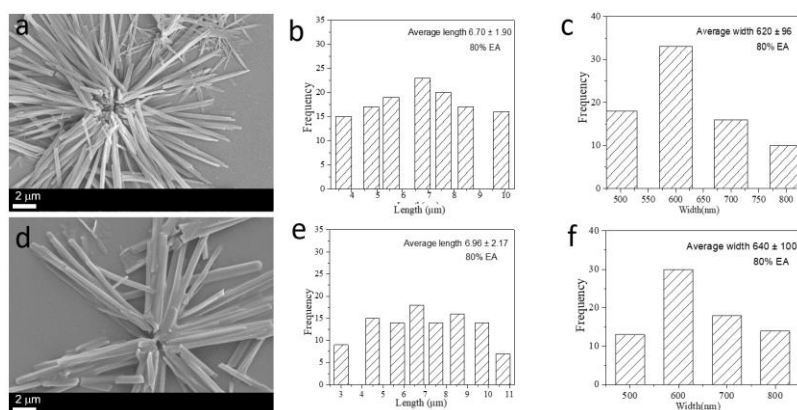


Figure S21. SEM images of cage 1 (10 μM) in DCM/EA mixture with 80% EA recorded at different aging time: (a-c) 120 and (d-f) 240 min.

1.22 Elemental mapping analysis of microneedles/microflowers

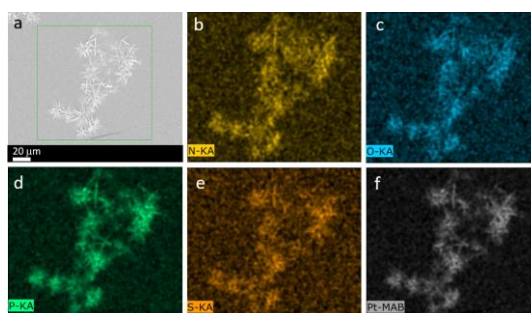


Figure S22. SEM and Elemental mapping analysis of microneedles/microflowers.

1.23 Microneedles/microflowers obtained at different temperature

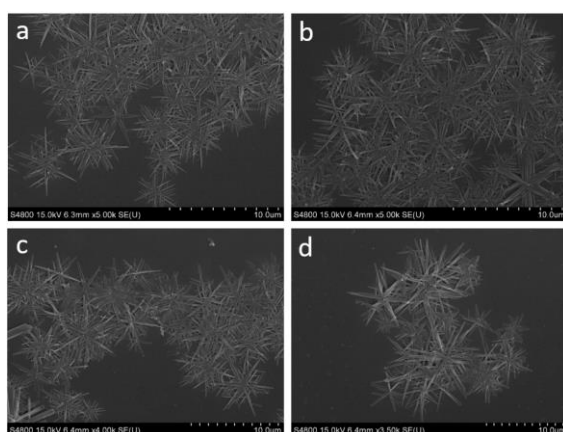


Figure S23. SEM images of cage 1 (10 μM) in DCM/EA mixture at different temperature: (a-b) 0 °C and (c-d) 30 °C.

1.24 Chemical structure of lysine-modified perylene

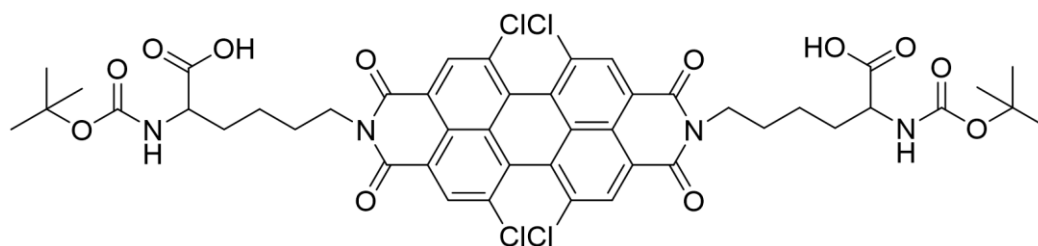


Figure S24. Chemical structure of lysine-modified perylene.

1.25 Histograms of the size distribution of microflowers formed in 80% EA

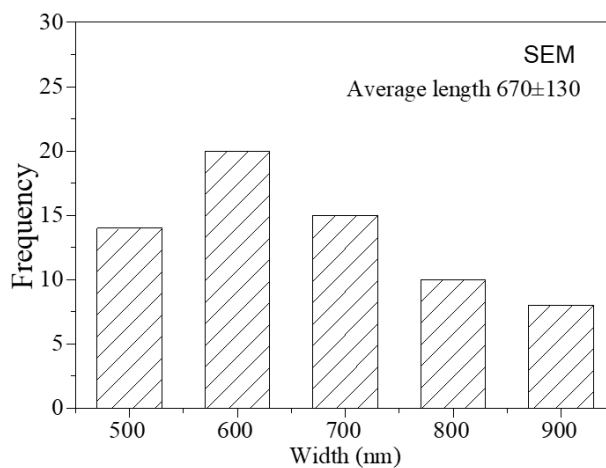


Figure S25. Histograms of the size distribution (width) of needle-based microflowers by cage 1 (10 μ M) in a DCM/EA mixture with 80% EA.

1.26 Optical and polarized images of needle-based flowers formed by the coassembly of cage 1 and perylene



Figure S26. Optical (a) and polarized (b) images of needle-based flowers contained lysine-modified perylene. (c) Corresponding histogram.

1.27 SAXS profile of needle-based flowers formed by the coassembly of cage 1 and perylene

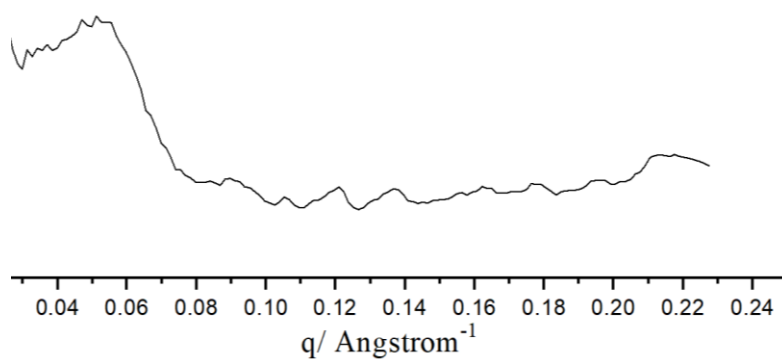


Figure S27. Corresponding SAXS profile of cage 1 and lysine-modified perylene in DCM/EA mixture with 80% EA.

1.28 ³¹P{¹H}NMR spectra microflowers redispersed in DCM.

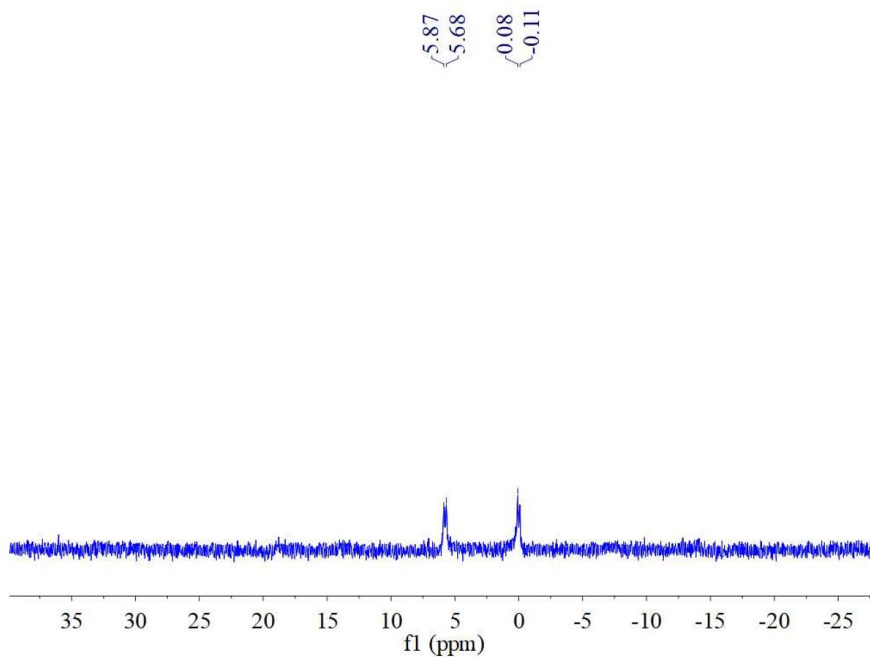


Figure S28. ³¹P{¹H}NMR spectra of perylene-contained microflowers redispersed in DCM.

1.29 $^1\text{H-NMR}$ of cage **1**, perylene, and the mixture of cage **1** and perylene

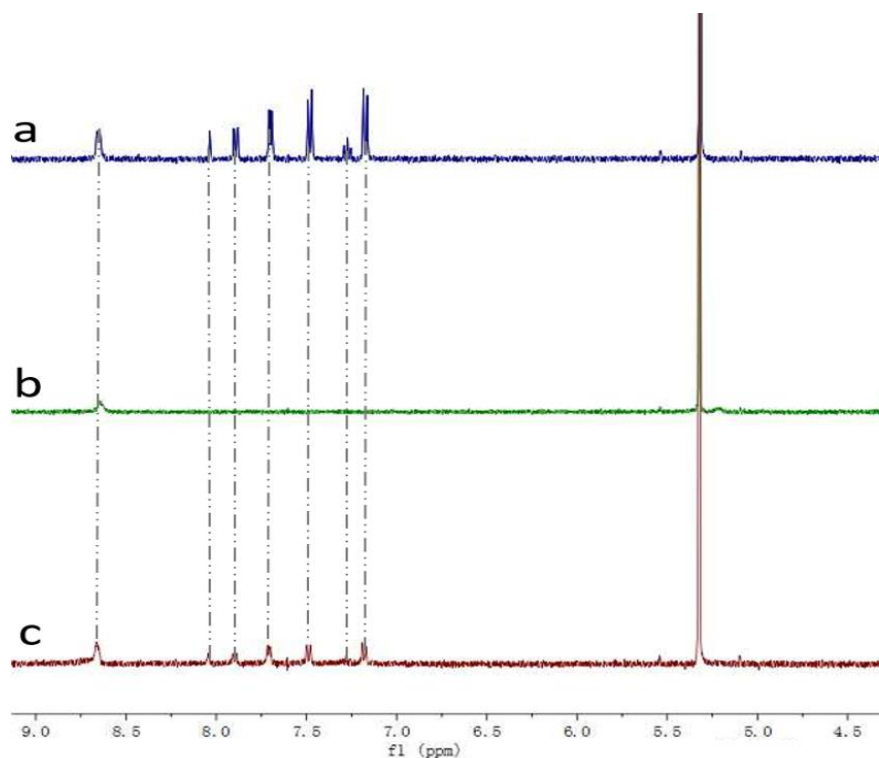


Figure S29. $^1\text{H-NMR}$ of (a) cage **1**, (b) lysine-modified perylene, and (c) cage **1** and lysine-modified perylene (400 Hz, CD_2Cl_2).

1.30 Fluorescence microscopy images of the chlorophyll-a contained assemblies

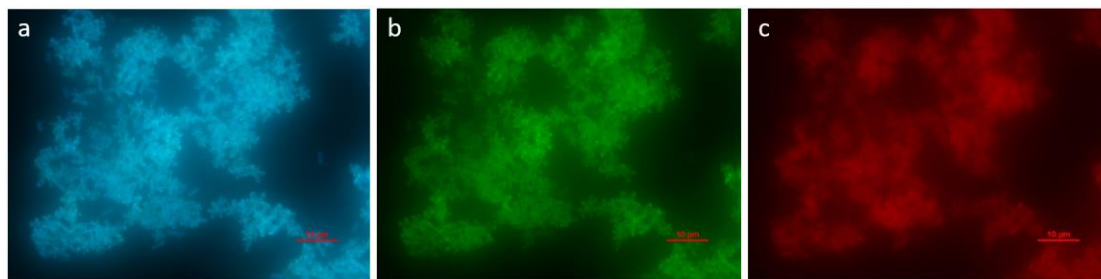


Figure S30. Fluorescence microscopy images of the chlorophyll-a contained assemblies under (e) ultraviolet-light excitation, (f) blue-light excitation and (g) green-light excitation.

1.31 $^1\text{H-NMR}$ of cage **1**, chlorophyll-a, and the mixture of cage **1** and chlorophyll-a

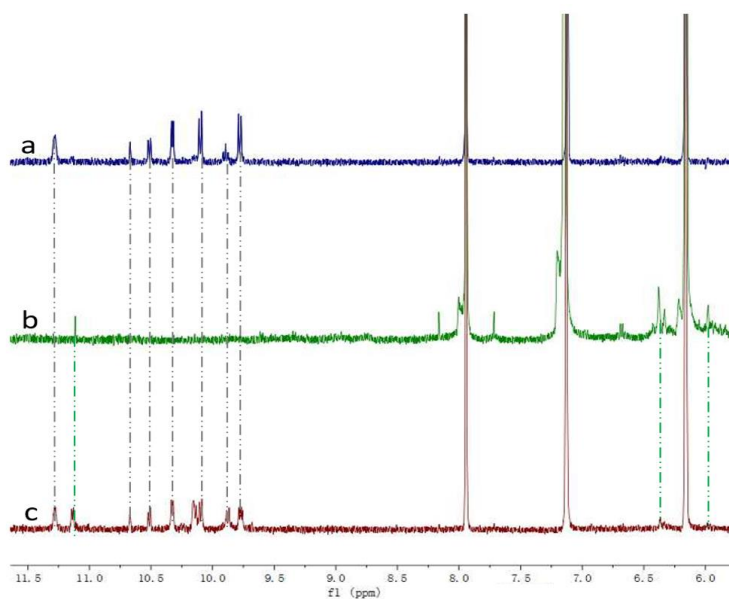


Figure S31. $^1\text{H-NMR}$ of (a) cage **1**, (b) chlorophyll-a, and (c) cage **1** and lysine-modified chlorophyll-a (400 Hz, $\text{CD}_2\text{Cl}_2/\text{Ethanol-}d^6=2:1$).

1.32 Fluorescence microscopy images of the Vitamin B_{12} contained assemblies

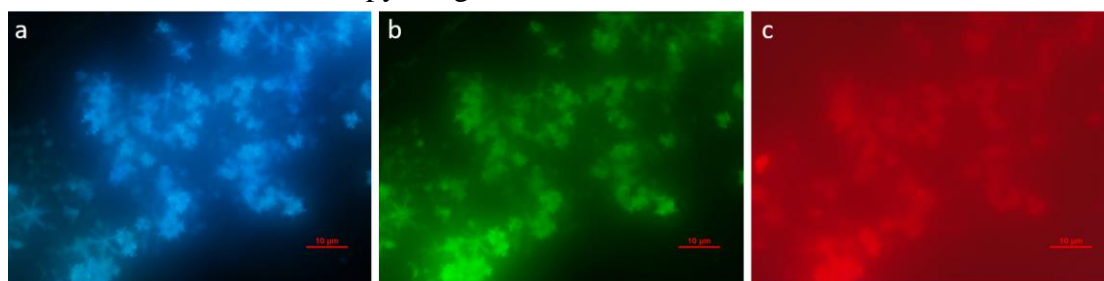


Figure S32. Fluorescence microscopy images of the Vitamin B_{12} contained assemblies under (e) ultraviolet-light excitation, (f) blue-light excitation and (g) green-light excitation.

1.33 $^1\text{H-NMR}$ of cage **1**, Vitamin B₁₂, and the mixture of cage **1** and Vitamin B₁₂

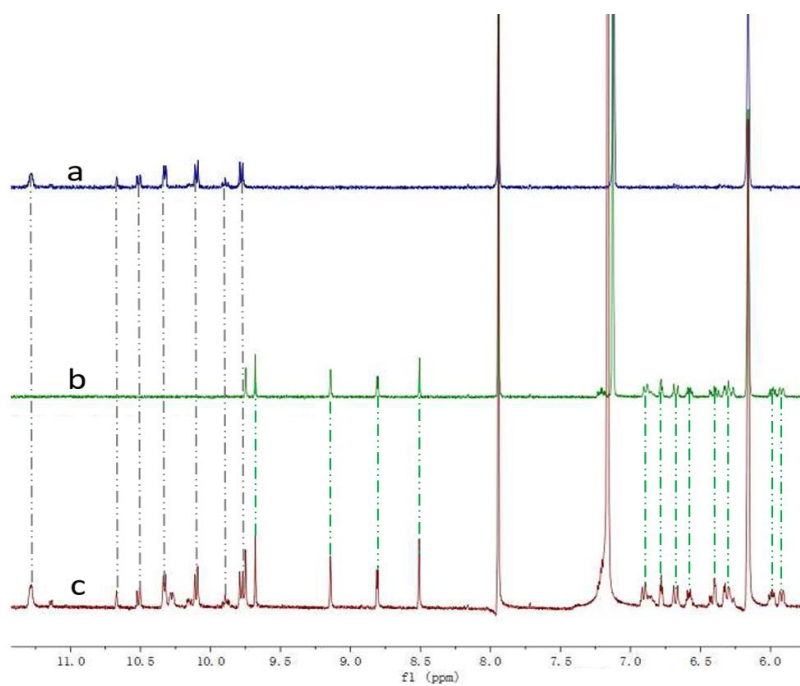


Figure S33. $^1\text{H-NMR}$ of (a) cage **1**, (b) Vitamin B₁₂, and (c) cage **1** and lysine-modified Vitamin B₁₂ (400 Hz, $\text{CD}_2\text{Cl}_2/\text{Ethanol-d}^6=2:1$).