Electronic Supplementary Material (ESI) for Chemical Communications.

Folding of two-dimensional nanoparticle superlattices enabled by emulsion-confined supramolecular co-assembly

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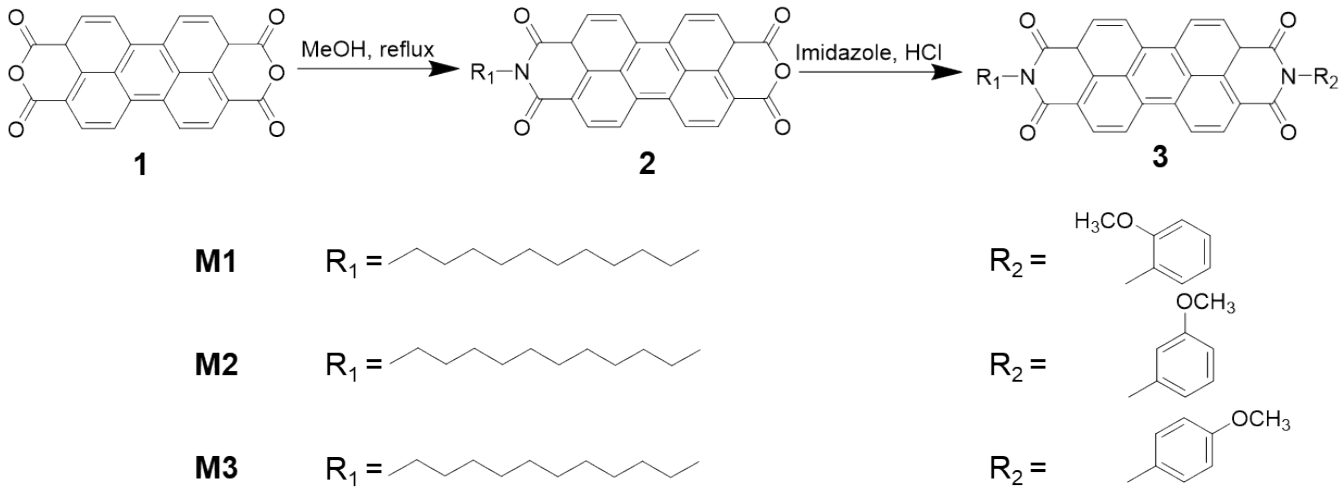
Experimental Procedures

Materials

All chemicals were used as received without any further purification: perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA, Sigma-Aldrich, 97%), 1-dodecylamine (TCI, 99.7%), methanol (Fuyu, 99%), hydrochloric acid (Fuyu, 37%), imidazole (Sigma-Aldrich, 99%), 2-Methoxyaniline (Aladdin, 98%), 3-Methoxyaniline (Aladdin, 98%), 4-Methoxyaniline (Aladdin, 97%), toluene (Fuyu, 99.5%), acetone (Fuyu, 99.5%), chloroform (Fuyu, 99.5%), ethanol (≥99%), chloro(triphenylphosphine)gold (Sigma-Aldrich, 99%), 1-dodecanethiol (DDT, Sigma-Aldrich, 99%), 1-octadecanethiol (Sigma-Aldrich, 99%), 1-decanethiol (Sigma-Aldrich, 99%), Borane *tert*-butylamine (TBAB, Sigma-Aldrich, 98%), dodecyltrimethylammonium bromide (DTAB, TCI, 99%).

Synthesis of molecules M1, M2 and M3.[1]



Scheme S1. The synthesis of molecules **M1**, **M2** and **M3.**

Molecule 2. 200 mg of perylene-3,4,9,10-tetracarboxylic acid dianhydride (**1**) and 1 g of 1-dodecylamine were mixed in 30 mL of methanol and refluxed for 7 hours. The resulting mixture was cooled to room

temperature and acidified by 20 mL of concentrated HCl. After stirring overnight, the resulting red solid was collected by vacuum filtration through a 0.45 μm membrane filter. The solid was washed thoroughly with methanol and distilled water until the pH of the washings turned neutral. The collected solid was then dried under vacuum at 60 °C. This raw product was not further purified before using for the next step of synthesis.

M1. The mixture containing compound **2** (110 mg), 2-methoxyaniline (120 mg) and imidazole (6 g) were heated to 145 °C and stirred for 5 hours under N_2. The resulting mixture was cooled to room temperature and dispersed in 50 mL of ethanol, followed by addition of 30 mL of concentrated HCl. After stirring overnight, the resulting red solid was collected by vacuum filtration through a 0.45 μm membrane filter, followed by thoroughly washing with ethanol and distilled water. The raw product was purified by column chromatography (silica, chloroform: acetone = 100:1) to afford compound **M1** (47 mg, 35% in the yield).

M1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58-8.74 (m, 8H), 7.47-7.53 (m, 1H), 7.31-7.36 (m, 1H), 7.10-7.18 (m, 2H), 4.18-4.24 (t, 2H), 3.81 (s, 3H), 1.72-1.81 (m, 2H), 1.02-1.35 (m, 18H), 0.86-0.89(t, 3H). MALDI-TOF-MS: (*m/z*) = 666.612.

M2, M3. Molecules **M2** and **M3** were synthesized by the above molecule **M1** method. The pure compounds of **M2, M3** were obtained through running column chromatography on a silica gel column (eluent, chloroform: acetone = 100: 1). The pure target compounds as obtained were confirmed by MALDI-TOF-MS and ^{1}H NMR as below.

M2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.77 (m, 8H), 7.48-7.52 (m, 1H), 6.89-7.08 (m, 3H), 4.18-4.24 (t, 2H), 3.86 (s, 3H), 1.73-1.80 (m, 2H), 1.02-1.35 (m, 18H), 0.86-0.89(t, 3H). MALDI-TOF-MS: (*m/z*) = 666.496.

M3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62-8.76 (m, 8H), 7.27-7.31 (m, 2H), 7.08-7.12 (m, 2H), 4.18-4.24 (t, 2H), 3.90 (s, 3H), 1.72-1.81 (m, 2H), 1.02-1.35 (m, 18H), 0.86-0.89(t, 3H). MALDI-TOF-MS: (*m/z*) = 666.773.

Synthesis of Au NPs.[2] In a typical synthesis of Au NPs capped with thiol, a precursor solution of toluene (25 mL) and chloro (triphenylphosphine) gold (0.124 g) was prepared in a three-neck flask (100 mL) and heated to 100 °C magnetically stirred under N_2 flow for 10 min. A reducing solution containing 0.300 g of TBAB, toluene (3 mL) and 1-dodecanethiol (2 mM) was mixed at 70 °C by sonication and injected into the precursor solution. The reduction was instantaneously initiated and the solution changed to a deep purple color within 5 s. The mixture was allowed to react at 100 °C for 5 min before acetone (60 mL) was added to precipitate the Au nanocrystals. The Au NPs was collected by centrifugation (8000 rpm, 3 min), washed with acetone and redispersed in chloroform. Au NPs with different size were prepared by changing the amount of TBAB and thiol. The diverse amount of TBAB and thiol as described in Table S1.

Table S1. Au NPs with different sizes and types.

Entry	TBAB / mg	Types of Thiol	Thiol / mg
Au4@C10	400	1-decanethiol	350
Au4@C12	400	1-dodecanethiol	400
Au4@C18	400	1-octadecanethiol	600
Au6@C18	100	1-octadecanethiol	150
Au7@C18	40	1-octadecanethiol	150

Emulsion confined assembly of PDI molecules.[3] For a typical self-assembly experiment, 0.3 mg of PDI molecules was dissolved in 0.6 mL of chloroform, followed by adding 1.2 mL of dodecyltrimethylammonium bromide (DTAB) aqueous solution with a concentration of 20 g L^{-1}. The resulting emulsion was severely agitated by a vortex for 60 s. The emulsion was then heated to 60 °C

and kept at this temperature for 30 min to evaporate the inner organic phase. After the suspension cooled to room temperature, the supernatant was removed by centrifugation. The resulting molecular assemblies was redispersed in 1 ml of deionized water.

Emulsion confined assembly of PDI molecules and NPs. For a typical self-assembly experiment, 0.2 mg of PDI molecules and desired concentration of nanocrystals were dispersed in 0.6 mL of chloroform, followed by adding 1.2 mL of DTAB aqueous solution with a concentration of 20 g L^{-1}. The resulting mixture was emulsified under a vortex mixer for 1 min. The resulting emulsion was heated to 60 °C and kept at this temperature for 30 min to evaporate the inner chloroform phase. The suspension was then allowed to cool to room temperature. The resulting assemblies were redispersed in 1 ml of deionized water.

Light-induced water evaporation. A certain mass of the assemblies was added to a weighing flask containing 10 ml of deionized water at room temperature. It is placed on an analytical balance and then irradiated by a light source for a certain period of time to record the quality change.

Structural characterizations. The morphologies and microstructures of the as-prepared samples were inspected by the transmission electron microscopy (TEM, HT-7700, accelerating voltage 200 kV) and scanning electron microscopy (FE-SEM, ZEISS SUPRATM 55). Small angle X-ray diffraction (XRD) were recorded using a SmartLab 9KW X-ray power diffractometer. UV-Vis absorption spectra of the samples were obtained by a UV-1900 (Shimadzu) UV-Vis spectrometer with quartz cells. ^{1}H NMR spectrum were recorded on a 400 MHz Bruker Avance spectrometer. MS spectrum were recorded on the Bruker Microflex mass spectrometer. AFM characterization was performed on a Bioscope Resolve Atomic Force Microscopy (Bruker).

DFT calculations. Geometry optimizations of the single molecule **M1**, **M2**, and **M3** at the B3LYP/6-31G (d) level of theory were performed with Gaussian 09. Further geometry optimizations of stacked dimers were carried out at M062X/6-31G (d) level. The alkyl chains were omitted during calculations.

Results and Discussion

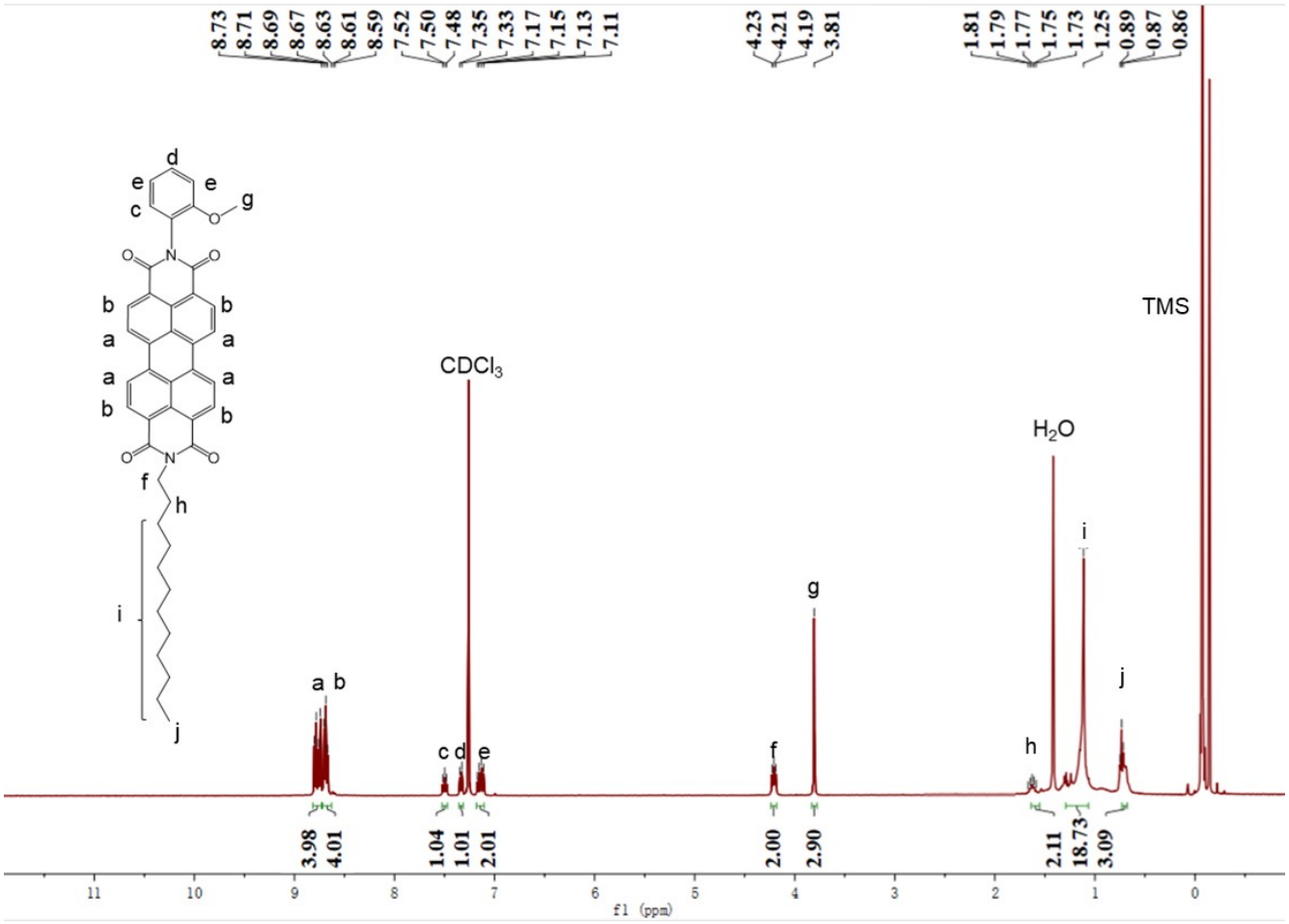


Figure S1. ^{1}H NMR spectrum of **M1**.

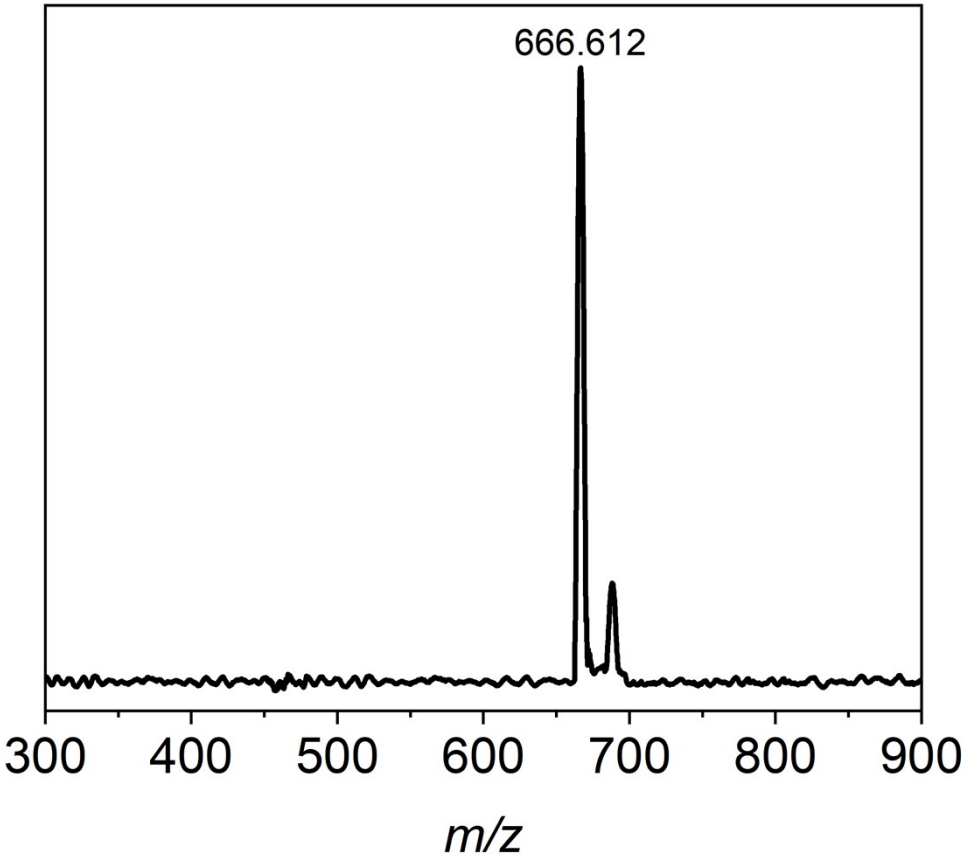


Figure S2. MALDI-TOF-MS spectrum of **M1**.

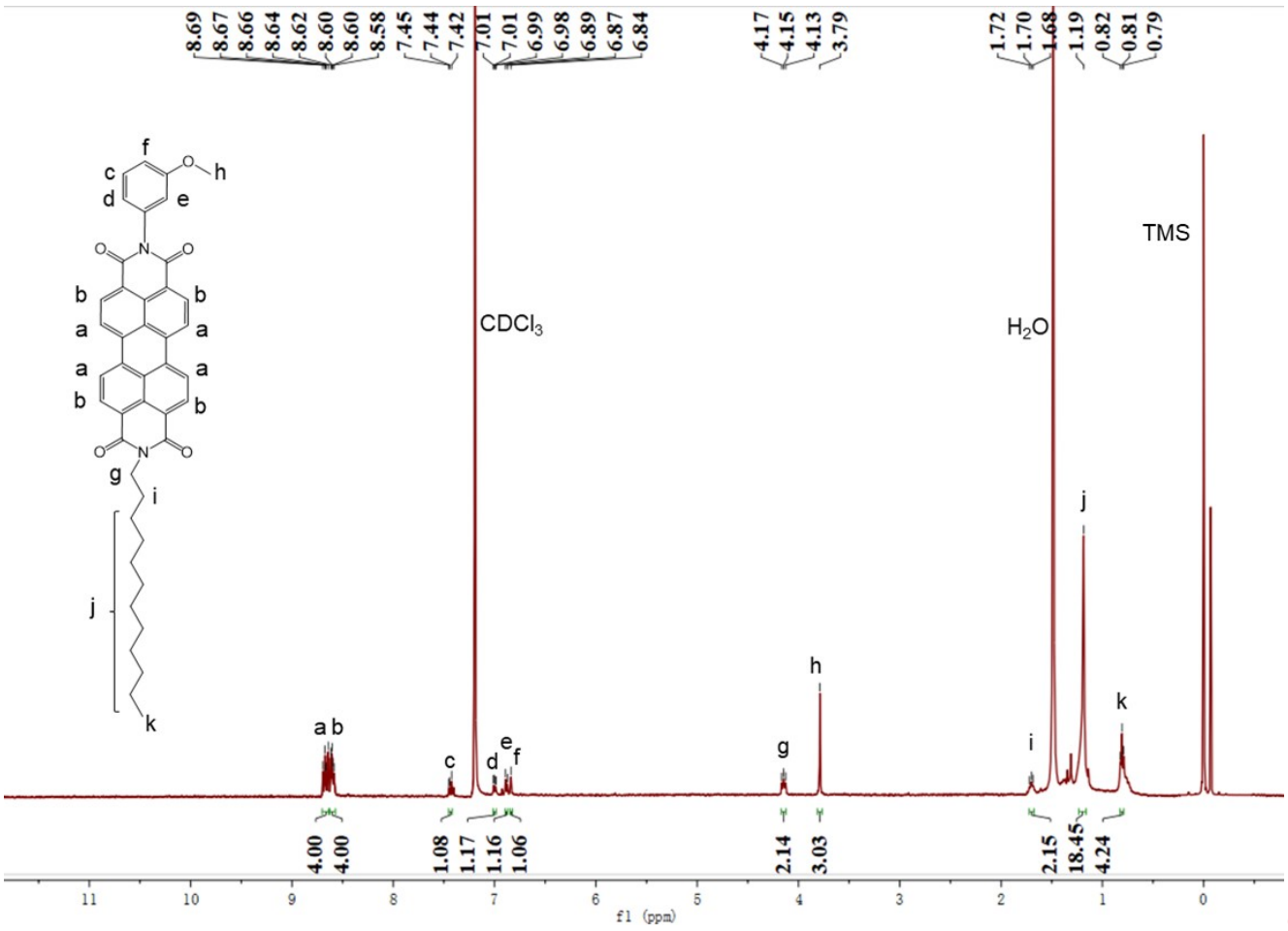


Figure S3. ^{1}H NMR spectrum of **M2**.

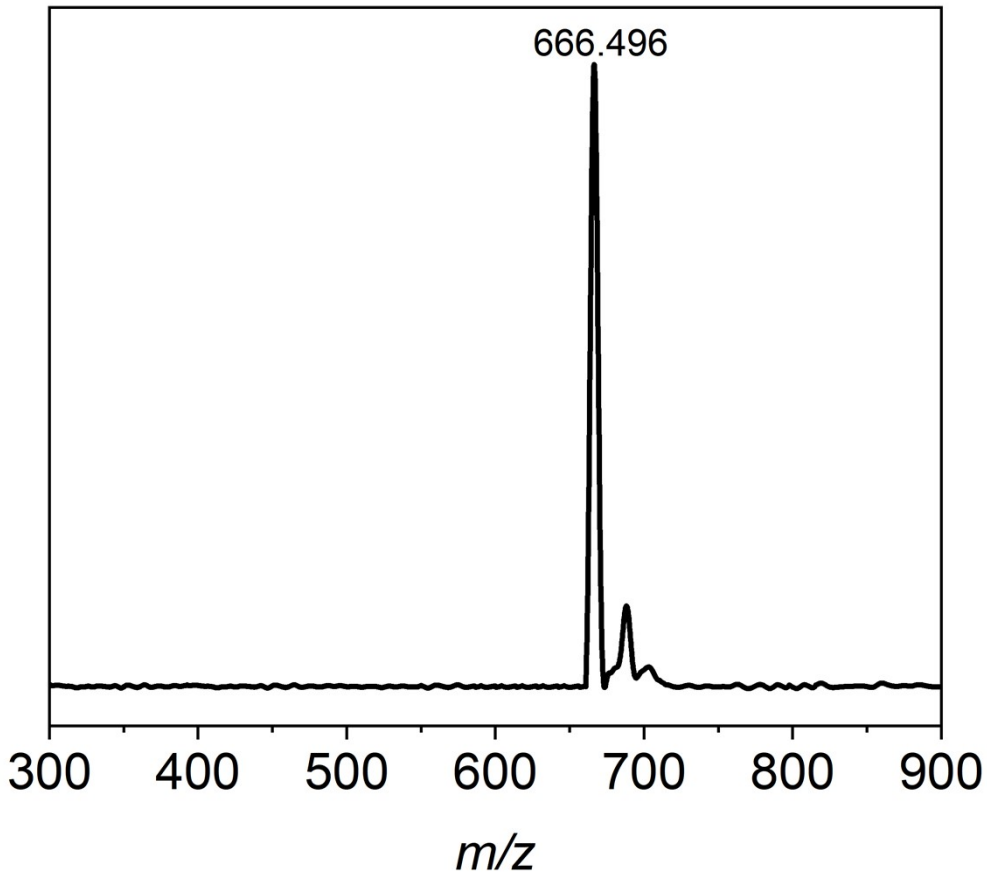


Figure S4. MALDI-TOF-MS spectrum of **M2**.

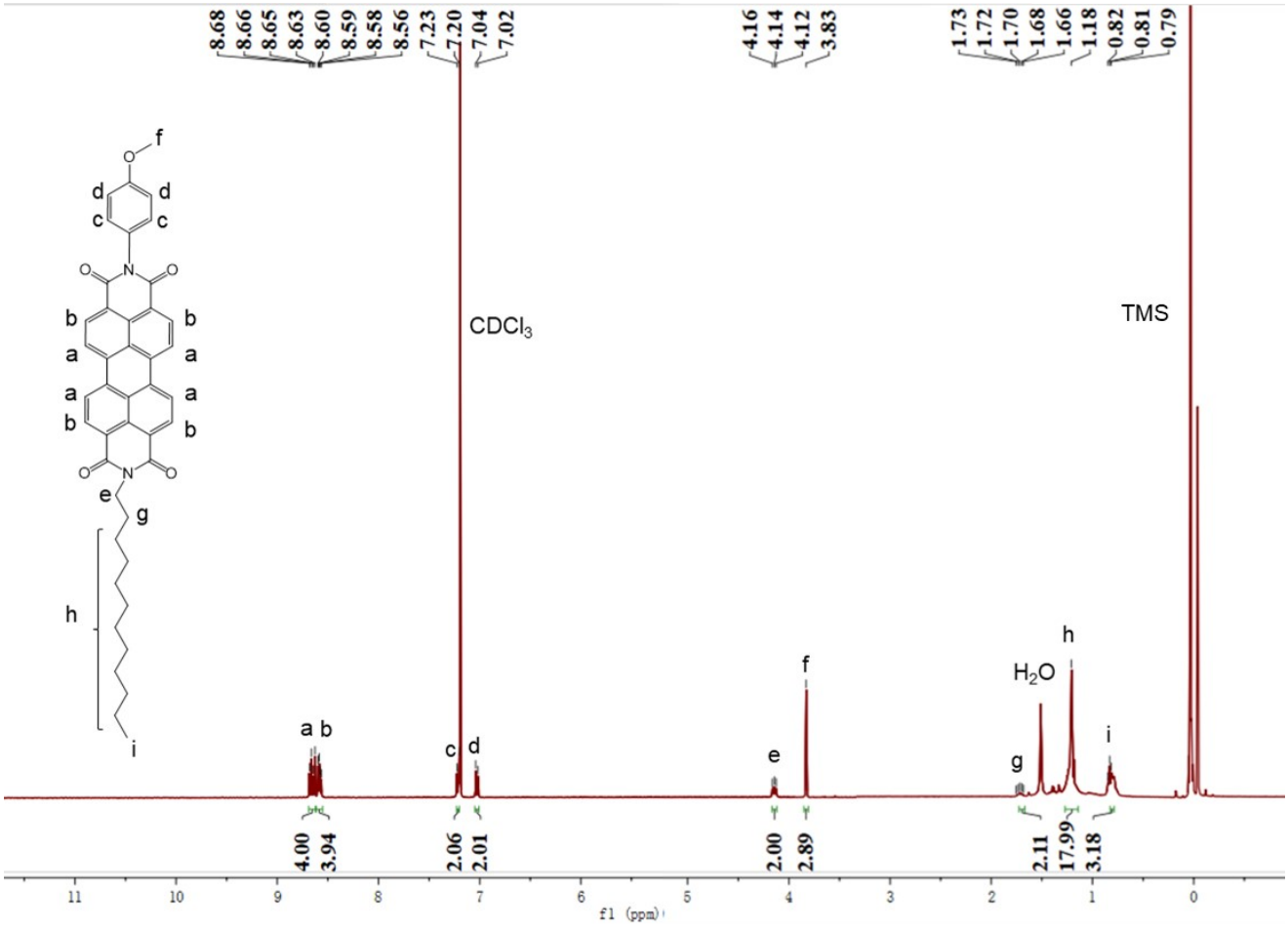


Figure S5. ^{1}H NMR spectrum of **M3**.

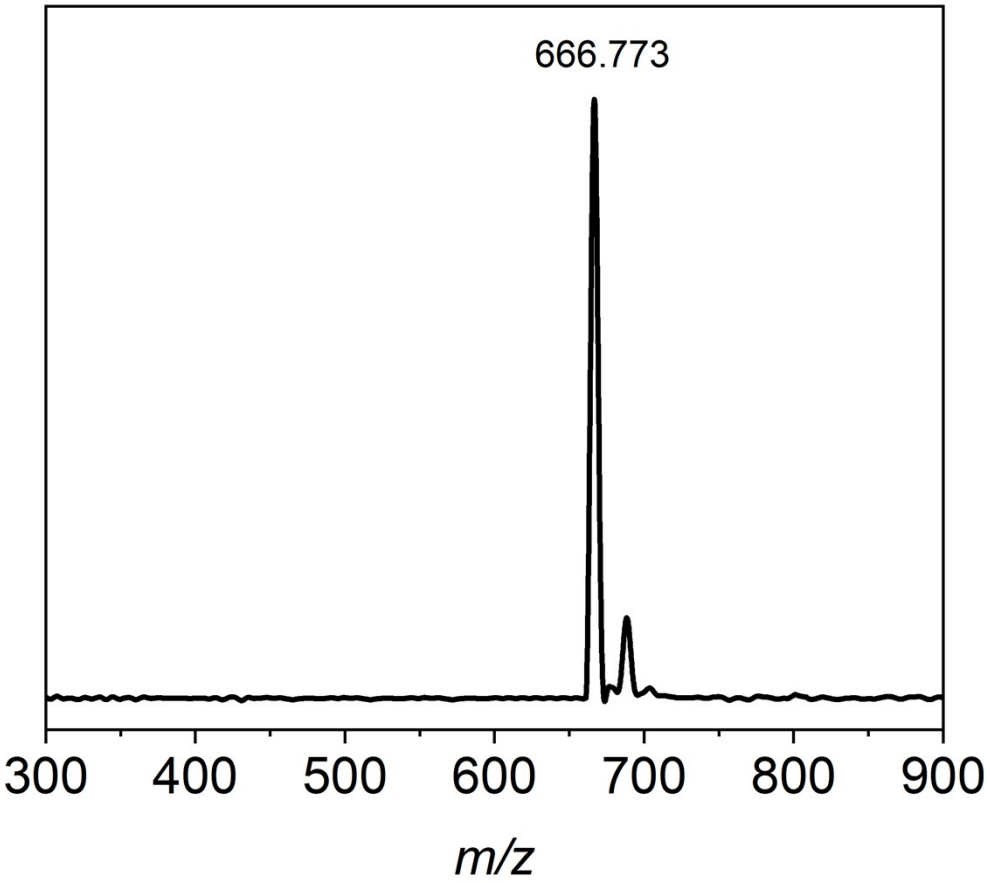


Figure S6. MALDI-TOF-MS spectrum of **M3**.

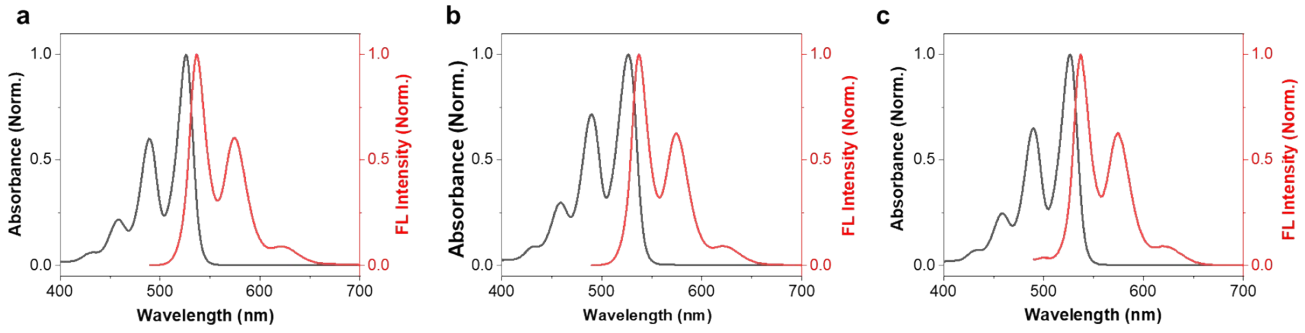


Figure S7. The UV-vis absorption spectra and fluorescence spectra of monomeric **M1** (a), **M2** (b) and **M3** (c).

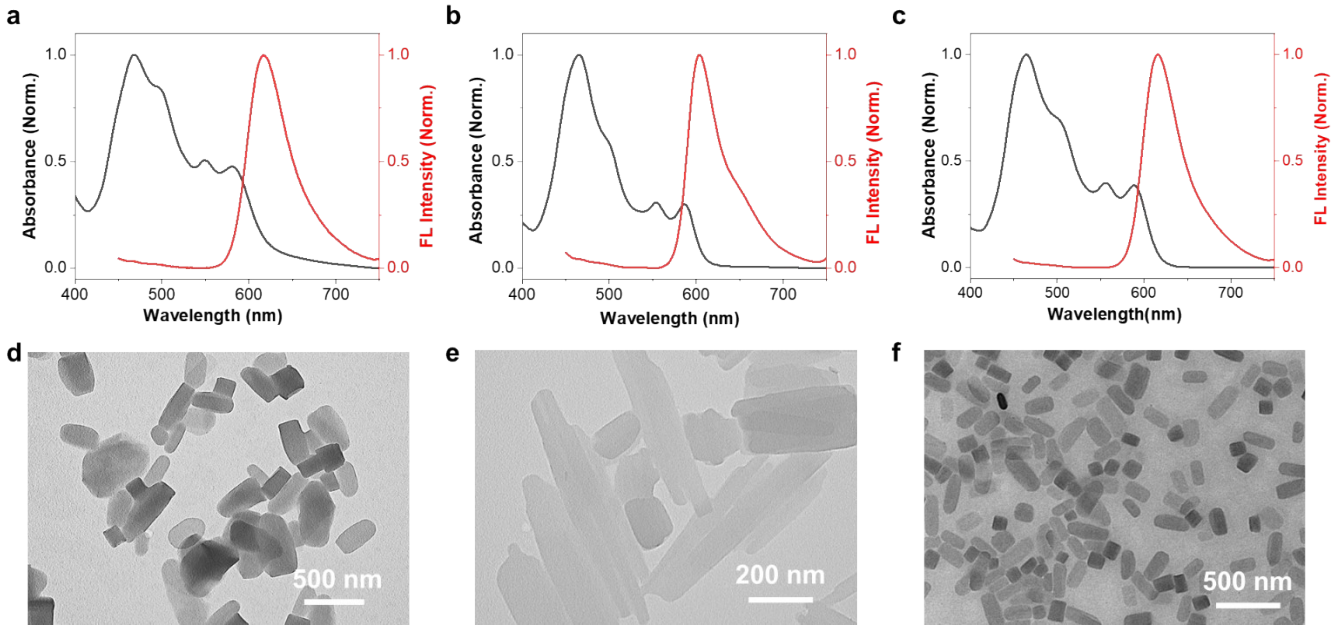


Figure S8. The UV-vis absorption spectra and fluorescence spectrum of **M1** (a), **M2** (b) and **M3** (c) assemblies. TEM images of **M1** (d), **M2** (e) and **M3** (f) assemblies.

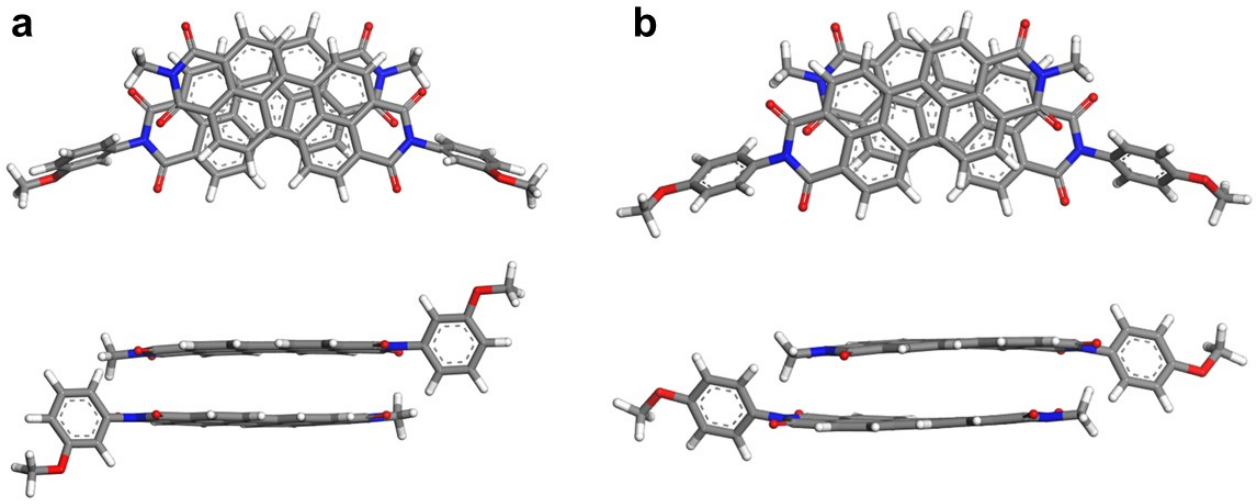


Figure S9. Geometry-optimized dimer structures obtained from DFT calculations of **M2** (a) and **M3** (b). Dodecyl groups are replaced by methyl groups for simplicity.

Table S2. Summarized table of the structural information measured from the DFT calculation.

Isomers	*L*-offset (Å)	*T*-offset (Å)	$d_{\pi\text{-}\pi}$ (Å)	ϑ (°)
M2	1.08	0.15	3.45	148.70
M3	1.83	0.00	3.36	146.81

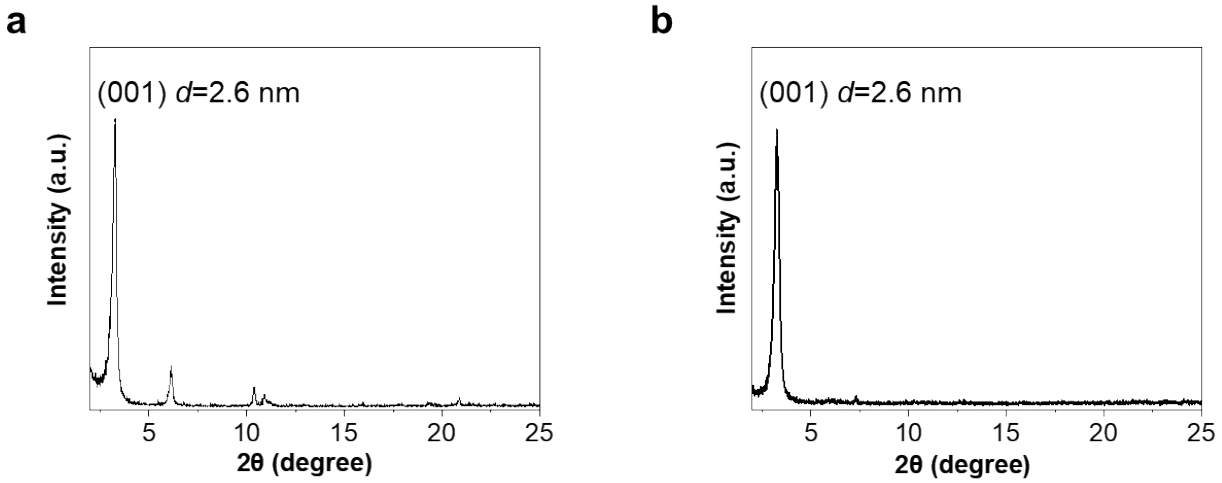


Figure S10. XRD patterns of **M2** assemblies (a), **M3** assemblies (b).

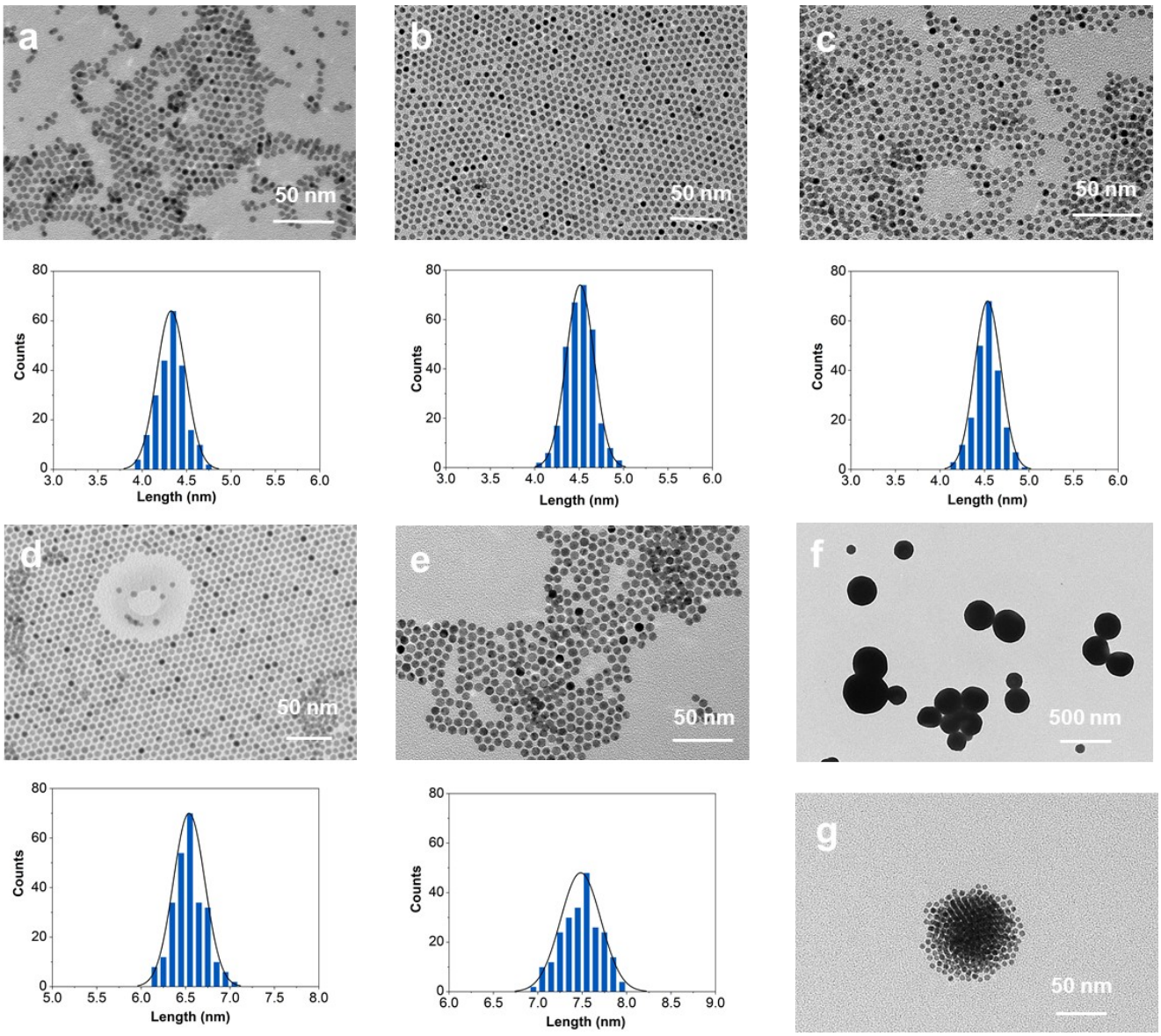


Figure S11. TEM images and size distribution of **Au4@C10** (a), **Au4@C12** (b), **Au4@C18** (c),, **Au6@C18** (d), **Au7@C18** (e) NPs, respectively. (f), (g) TEM image of Au nanoparticle clusters assembled in the emulsion droplets.

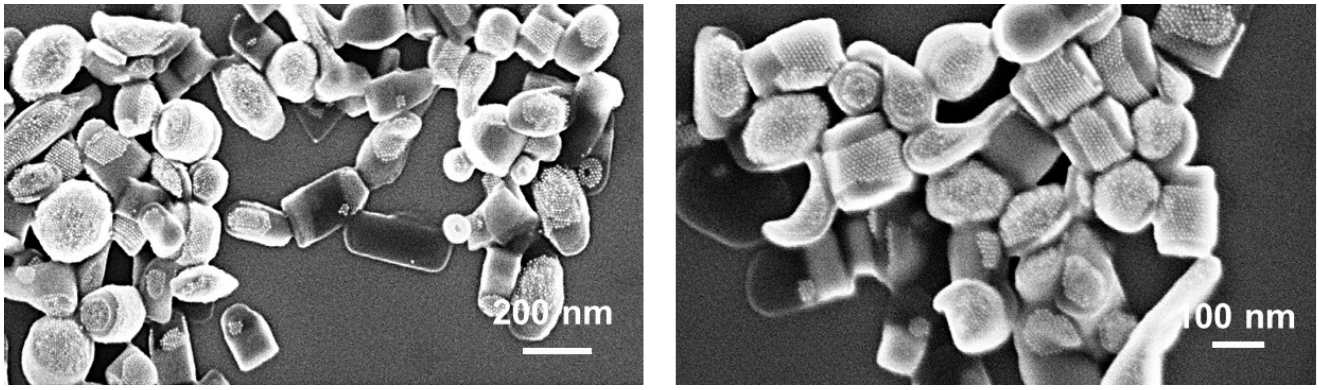


Figure S12. SEM images of **M1/Au4** assemblies.

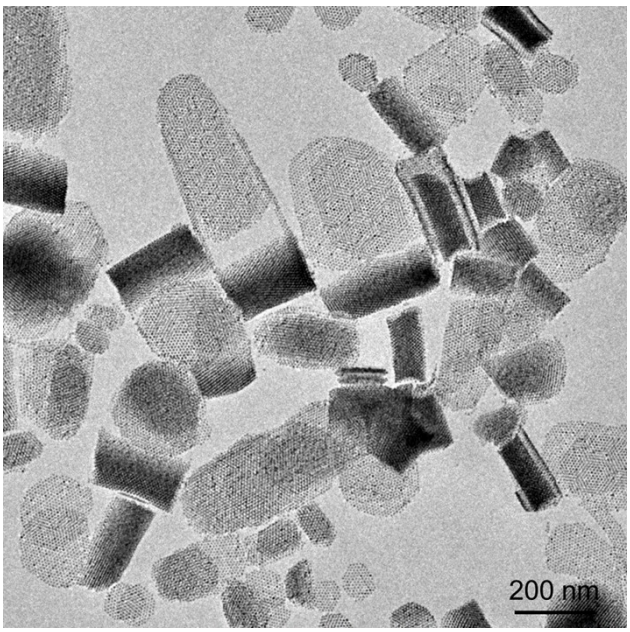


Figure S13. TEM images of the **M1/Au4** (1/1) coassemblies after aging over 2 months at room temperature. The assemblies were dispersed in water and sealed in a glass vial (5 ml).

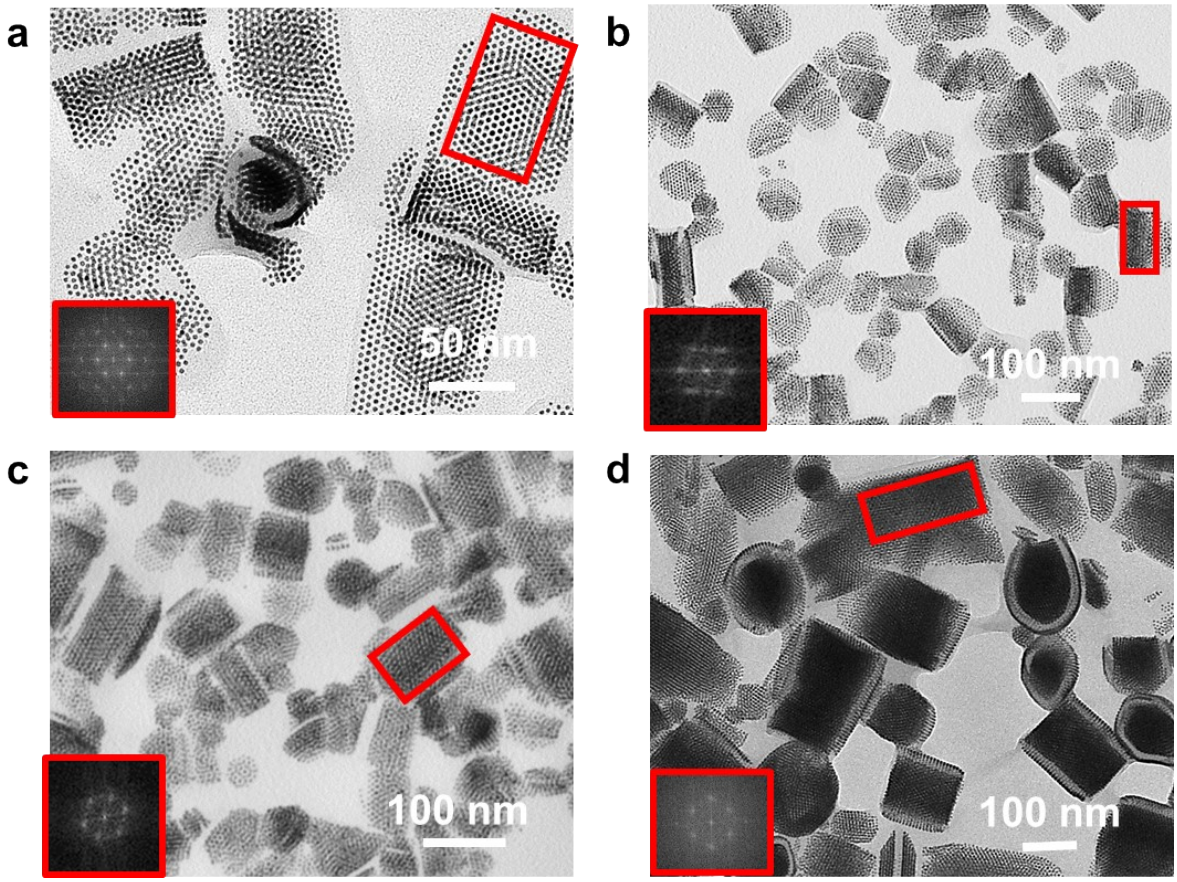


Figure S14. TEM images of **M1/Au4** assemblies with m_{M1}/m_{Au} = 1/1 (a), 1/2 (b), 1/3 (c), 1/4 (d). Insets are the corresponding FFT patterns.

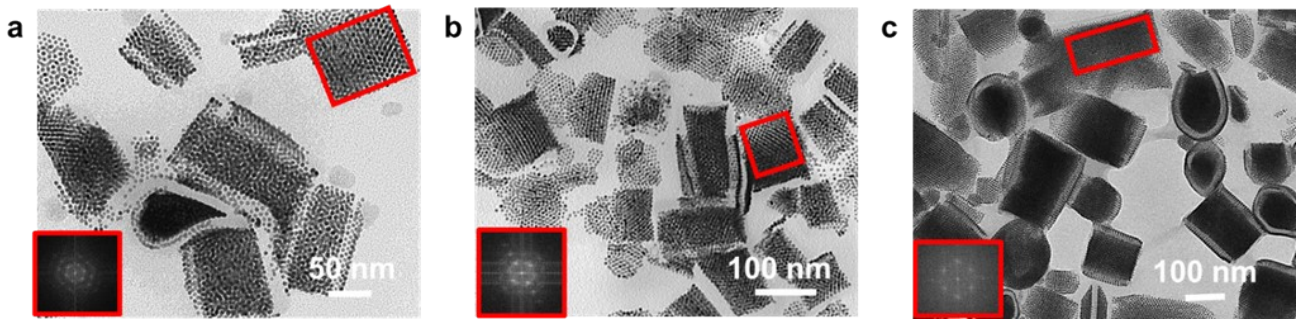


Figure S15. TEM images of **M1/Au4** assemblies with **C10** (a), **C12** (b), **C18** (c) of aliphatic chains coated on the **Au4** NPs. Insets are the corresponding FFT patterns.

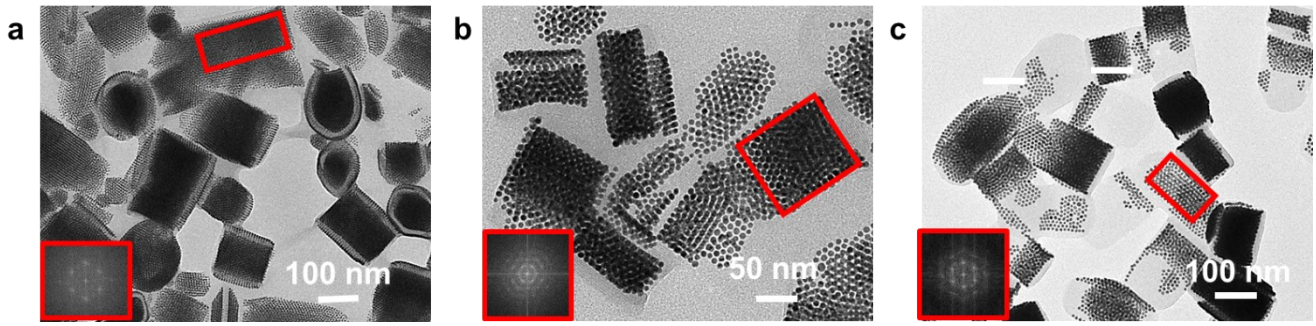


Figure S16. TEM images of **M1/Au** assemblies with the size of **Au4** (a), **Au6** (b), **Au7** (c). Insets are the corresponding FFT patterns.

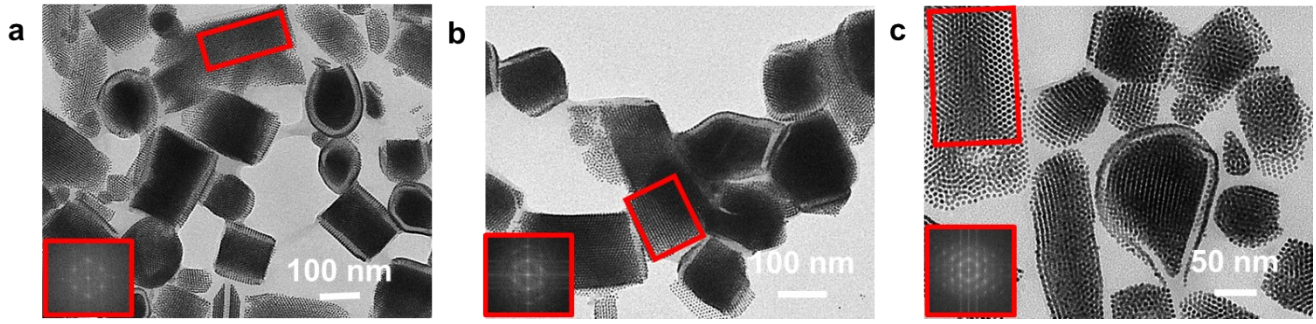


Figure S17. TEM images of assemblies with **M1/Au4** (a), **M2/Au4** (b), **M3/Au4** (c). Insets are the corresponding FFT patterns.

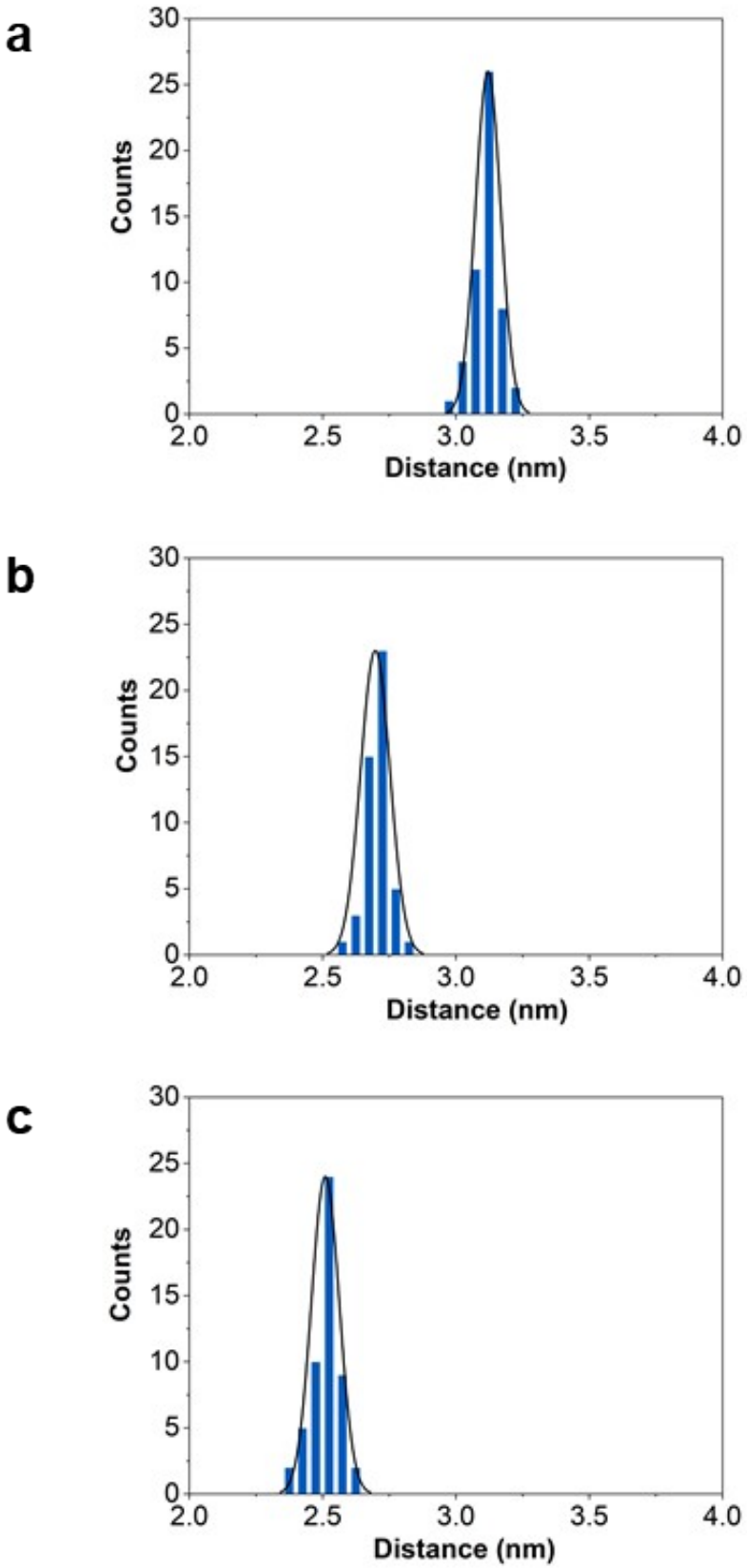


Figure S18. Statistical interparticle distance between NPs of **Au4@C18** (a), **Au6@C18** (b), **Au7@C18** (c) in the assemblies.

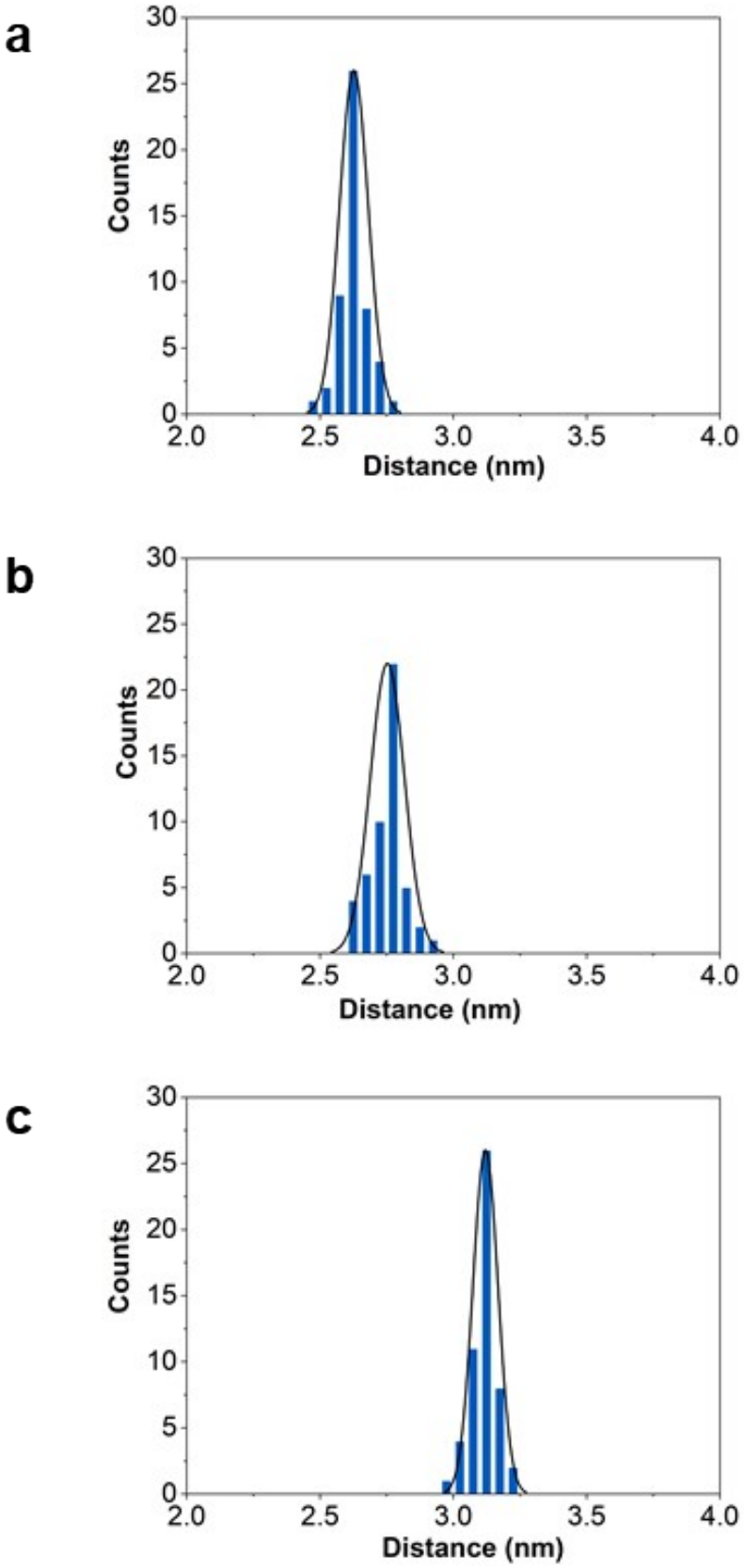


Figure S19. Statistical interparticle distance between NPs of **Au4@C10** (a), **Au4@C12** (b), **Au4@C18** (c) in the assemblies.

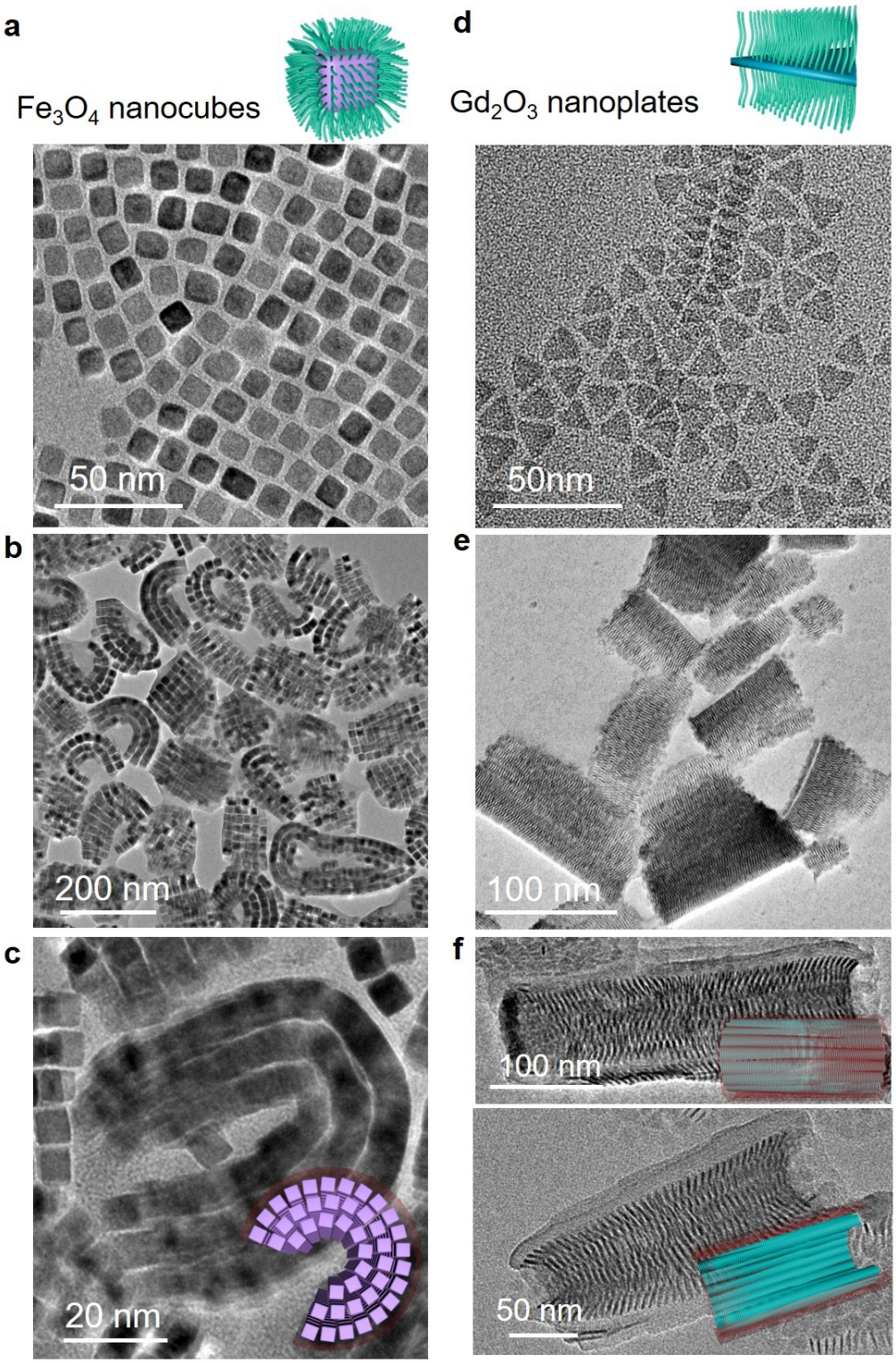


Figure S20. TEM images of Fe_3O_4 nanocubes (a) and their co-assemblies with **M1** molecules (b-c); TEM images of Gd_2O_3 nanoplates (d) and their co-assemblies with **M1** molecules (e-f). The cartoon illustrations were included in (a, c, d, f).

References

1. Y. Che, X. Yang, G. Liu, C. Yu, H. Ji, J. Zuo, J. Zhao, L. Zang, *J. Am. Chem. Soc.*, **2010**, *132*, 5743-5750.
2. N. Goubet, H. Portales, C. Yan, I. Arfaoui, P. A. Albouy, A. Mermet, M. P. Pileni, *J. Am. Chem. Soc.*, **2012**, *134*, 3714-3719.
3. Y. Gong, Z. Cao, Z. Zhang, R. Liu, F. Zhang, J. Wei, Z. Yang, *Angew. Chem. Int. Ed.*, **2022**, 10.1002/anie.202117406.