Electronic Supporting Information

Tunable Low-Dimensional Self-Assembly of H-Shaped Bichromophoric

Perylenediimide Gemini in Solution

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Materials. All the chemicals were purchased from Sigma-Aldrich, Merck, Alfa Aesar and TCI suppliers, and were used as received unless otherwise described. Specifically, perylene-3,4:9,10-tetracarboxylic dianhydride (97%), bromine (99.99%), tin chloride dihydrate $(SnCl_2 \cdot 2H_2O)$ 98%), potassium tert-butoxide 98%), (t-BuOK, tris(dibenzylideneacetone)-dipalladium(0) ($Pd_2(dba)_3$, 97%), 1,3-bis(diphenylphosphino) -propane (dppp, 97%) and potassium thioacetate (98%) were purchased from Sigma-Aldrich. Dimethyl Formamide (DMF, HPLC), 1, 2-dichloroethane (DCE, 99.5 %), nitric acid (fuming, 100%), dichloromethane (CH₂Cl₂, anhydrous, 99.8%), tetrahydrofuran (THF, anhydrous, 99.9%), hexane (HPLC, 97%) and methanol (99.9%) were purchased from Merck. 2-Octyldodecylamine (97%) was purchased from TCI, cerium (IV) ammonium nitrate (98%) was purchased from Alfa Aesar. Anhydrous toluene was distilled over Na/benzophenone under nitrogen after pre-dried with Na overnight. All the self-assembly experiments were carried out using HPLC grade solvents. 200 mesh copper grids (ZB-C4000) with ultra-thin carbon support film with thickness ≤ 3 nm were purchased from Beijing Zhongxing Bairui Technology Co., Ltd. Silicon wafer (~ 0.25 cm²) was purchased from Shanghai Xinyang Semiconductor Materials Co., Ltd., which was pretreated with O_2 plasma for 20 min to make it more hydrophilic.

Characterization methods. Analytical thin layer chromatography (TLC) was carried out on silica gel coated substrates bought from Merck. Hydrogen and carbon Nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra were recorded on a Bruker Advance 300 NMR spectrometer with tetramethylsilane as the internal reference and chloroform-d (CDCl₃) as solvents under ambient temperature. NMR data were collected via chemical shift (ppm, CDCl₃ resonance as the external standard), multiplicity and integration. All the high-resolution mass spectra (HR-MS) were performed on a Waters Q-T of premier mass spectrometer using acetone as solvent. Ultraviolet–Visible (UV–vis) absorption UV-vis-NIR spectra were performed on Cary 5000 spectrophotometer. Photoluminescence (PL) spectra were carried out via a Cary Eclipse Fluorescence Spectrophotometer. Quartz cuvettes or plates were used for all the optical measurements. Atomic force microscope (AFM) observations were completed on a scanning probe microscope (AFM Asylum Research Cypher S, USA) operated via AC Mode Imaging under atmosphere by using Arrow-NCR-50-Silicon SPM-Sensor cantilevers (side: Alcoating, Coating: detector, force constant of 42 N m⁻¹). AFM samples were prepared via by drop-casting one drop (ca. 10 μ L) of the assembly solution onto silicon wafer which was placed on a piece of filter paper to remove most of the solvent, and then dried under vacuum for 4 h at room temperature (RT). Scanning electron microscope (SEM) images were collected on a JEOL/JSM-6340F under electric voltage of 5 kV. SEM samples were prepared by drop-casting 5 drops (dropped one drop, dried, dropped, ... repeated for 5 times, totally ca. 50 μ L) of the assembly solution onto silicon wafer, and then dried under vacuum for 4 h at room temperature (RT). Au spray was performed on the samples (30s) to enhance the contrast before test. Transmission electron microscopy (TEM) measurements were carried out on a JEM-2100 (JEOL Ltd., Japan) with accelerating voltage of 200 kV. TEM samples were prepared by dropping the assembly solutions (ca. 10 µL) onto an ultrathin carbon-coated copper grids which was placed on a silicon wafer to avoid spreading out of the solution, followed by drying under vacuum for 4 h at RT, and no staining treatment was applied for TEM samples. The d-spacings in SAED patterns were calibrated by gold nanoparticles standard. All the images were analyzed via the ImageJ software developed by the US National Institute of Health. For the statistical analysis, ca. 200 assemblies were carefully traced manually to determine the dimension distributions using ImageJ. Samples used for small and wide-angle X-ray scattering patterns (SAXS and WAXS) tests were prepared by SD method, in which 10 mg PDI-NH-PDI was dissolved in 1 mL toluene and then diffused into certain amount of hexane for 2 days. Afterwards, dropping the self-assembled dispersion on a cleaned glass substrate, and dried under vacuum before tests, which was fixed on the sample holder to perform test. SAXS and WAXS analyses were recorded on a Xenocs Nanoinxider with Cu-Ka microsource (40 mm, $\lambda = 1.5$ Å) at 30W under RT. Each collection was recorded using medium resolution (MR) for 15 min. All the photos were taken by a Cannon EOS 700D camera.

Synthesis of bromo perylene diimide (PDI-Br)¹



Scheme S1. Preparation of bromo perylene diimide (PDI-Br).

PDI was prepared according to the literature.² Perylene-3,4:9,10-tetracarboxylic dianhydride (5.1 mmol, 2.0 g) and 2-Octyldodecylamine (25.5 mmol, 5 eq., 7.6 g) were suspended in 30 mL DMF in a 250 mL 1-neck flask equipped with a condenser. The reaction mixture was degassed by argon bubbling, and then refluxed overnight under nitrogen atmosphere. After reaction, the solution was cooled to RT, and 30 mL hydrogen chloride (HCl) aqueous solution (1N) was added under stirring, the stirring was maintained for 10 min. The resulted precipitate was collected by filtration and treated by 30 mL potassium hydroxide (KOH) aqueous solution (1M) to remove the excess HCl. The precipitate was filtered again and washed with water until pH = 7 and dried under vacuum at RT. Purification by silica gel column chromatography using eluent of hexane/dichloromethane (DCM) (2/1, v/v) yielded PDI as as a dark red solid in 91% yield.

¹H NMR (300 MHz, CDCl₃, **Fig. S1**): δ 8.69–8.51 (d, 4H), 8.51–8.32 (d, 4H), 4.25–4.00 (d, 4H), 2.15–1.82 (m, 2H), 1.48–1.18 (m, 64H), 0.98–0.75 (t, 12H).

¹³C NMR (300 MHz, CDCl₃, **Fig.** S2): δ 163.51 (4C), 134.12 (4C), 131.15 (4C), 129.16 (2C), 126.03 (2C), 123.25 (4C), 122.84 (4C), 44.80 (2C), 36.75 (2C), 32.00 (6C), 31.85 (2C), 30.17 (4C), 29.74 (6C), 29.44 (4C), 26.62 (4C), 22.75 (6C), 14.18 (4C).

HR-MS (**Fig. S3**): m/z (%): 951.7011 (100) [M+H]⁺ (calcd. C₆₄H₉₁N₂O₄ = 951.6979).



Fig. S2. ¹³C NMR spectrum of PDI.



Fig. S3. HR-MS spectrum of PDI.

Preparation of PDI-Br.¹ A mixture of PDI (4 mmol, 2.9 g) and bromine (0.5mL, 10 mmol) in 60 mL of 1, 2-dichloroethane (DCE) was stirred at 80 °C in a closed round-bottom flask for 1 day. Afterwards, the excess of bromine was removed by saturated sodium thiosulfate aqueous solution via washing for 3 times. Then the organic phase was dried with anhydrous sodium sulfate (Na₂SO₄) and then evaporated under vacuum. The crude product was purified via silica gel column chromatography (eluent, hexane/DCM = 4/1, v/v), which afford bromo perylene diimide as a red solid in 89% yield.

¹H NMR (300 MHz, CDCl₃, **Fig. S4**): δ 9.82–9.69 (d, 1H), δ 9.01–8.82 (s, 1H), δ 8.75– 8.59 (d, 3H), δ 8.58–8.36 (d, 2H), δ 4.25–4.01 (d, 4H), δ 2.20–1.75 (m, 2H), δ 1.51–1.12 (m, 64H), δ 0.98–0.75 (t, 12H).

¹³C NMR (300 MHz, CDCl₃, **Fig.** S5): δ 163.65 (1C), 163.34 (1C), 163.24 (1C), 162.44 (1C), 139.07 (1C), 133.62 (1C), 133.25 (1C), 130.88 (4C), 130.44 (1C), 128.62 (1C), 128.43 (1C), 127.96 (1C), 127.76(1C), 126.71(1C), 123.53 (1C), 123.59 (1C), 123.39 (1C), 123.04 (1C), 122.83 (1C), 122.61 (1C), 120.96 (1C), 44.82 (2C), 36.70 (2C), 31.99 (6C), 31.81 (4C), 30.13 (2C), 29.41 (6C), 26.60 (2C), 22.75 (6C), 14.18 (4C).

HR-MS (**Fig. S6**): m/z (%): 1031.6075 (100) $[M+H]^+$ (calcd. C₆₄H₉₀N₂O₄81Br = 1031.6064).



Fig. S5. ¹³C NMR spectrum of PDI-Br.





Synthesis of amino perylene diimide (PDI-NH₂)³



Scheme S2. Preparation of amino perylene diimide (PDI-NH₂).

Preparation of nitro perylene diimide (PDI-NO₂). PDI- NO₂ was prepared according to the literature.³ Cerium (IV) ammonium nitrate (CAN, 1.2 g, 2.2 mmol), PDI (1.3 g, 1.8 mmol) and nitric acid (2.0 g, 31.7 mmol) were added into a 250 mL round-bottom flask, then 150 mL DCM was added. The resulted mixture was stirred at 25 °C under Ar₂ for 48 h. After reaction, the mixture was neutralized with 10% KOH and then extracted with DCM. The organic layer was dried and evaporated under vacuum. Afterwards, the crude

product was purified through silica gel column chromatography with eluent hexane/DCM (1/1, v/v) to afford nitro perylene diimide as a pink solid in 92% yield.

¹H NMR (300 MHz, CDCl₃, **Fig. S7**): δ 8.81–8.50 (m, 6H), δ 8.25–8.00 (d, 1H), δ 4.25– 4.01 (d, 4H), δ 2.15–1.81 (m, 2H), δ 1.51–1.02 (m, 64H), δ 0.92–0.75 (t, 12H).

¹³C NMR (300 MHz, CDCl₃, **Fig. S8**): δ 163.32 (1C), 163.01 (1C), 162.91 (1C), 162.09 (1C), 147.57 (1C), 135.38 (1C), 132.83 (2C), 131.39 (1C), 131.20 (1C), 129.21 (2C), 128.85 (1C), 127.92 (1C), 127.38 (1C), 126.46 (1C), 126.36 (2C), 124.82 (1C), 124.49 (1C), 124.12 (1C), 124.03 (1C), 123.86 (1C), 123.05 (1C), 45.07 (1C), 44.91 (1C), 36.68 (1C), 36.74 (1C), 32.00 (4C), 31.76 (2C), 30.13 (4C), 29.72 (8C), 29.43 (4C), 26.55 (4C), 22.75 (6C), 14.18 (4C).

HR-MS (Fig. S9): m/z (%): 996.6821 (100) [M+H]⁺ (calcd. C64H90N3O6=996.6830).



Fig. S7. ¹H NMR spectrum of PDI-NO₂.







Fig. S9. HR-MS spectrum of PDI-NO₂.

Preparation of amino perylene diimide (PDI-NH₂). PDI- NH₂ was prepared according to the literature³ described below. Tin chloride dihydrate (SnCl₂.2H₂O, 5.5 mmol, 1.3 g) and PDI-NO₂ (1.7 mmol, 1.7 g) were suspended in 50 mL tetrahydrofuran (THF) in 100 mL round-bottom flask. The mixture was stirred for 20 min and followed by refluxing under stirring for another 2 h. After that, THF was removed by the rotary evaporator, and the obtained crude product was dissolved in ethyl acetate and washed with 10% sodium hydrate (NaOH) solution for 3 times and then with brine for 3 times. The organic layer was collected and dried over anhydrous Na₂SO₄. Then the solvent in the filtrate was evaporated under vacuum. Purification via silica gel column chromatography with eluent hexane/DCM (3/1) containing 1% triethylamine to afford blue PDI-NH₂ in 84% yield.

¹H NMR (300 MHz, CDCl₃, **Fig. S10**): δ 8.75–8.61 (d, 1H), δ 8.59–8.41 (m, 2H), δ 8.38– 8.14 (m, 3H), δ 7.96–7.81 (s, 1H), δ 5.25–5.12 (s, 2H), δ 4.18–4.01 (d, 4H), δ 2.01–1.81 (m, 2H), δ 1.48–1.01 (m, 64H), δ 0.98–0.75 (t, 12H).

¹³C NMR (300 MHz, CDCl₃, **Fig. S11**): δ 163.92 (1C), 163.65 (1C), 163.43 (1C), 161.37 (1C), 146.07 (1C), 136.00 (1C), 134.86 (1C), 132.52 (1C), 131.50 (1C), 130.98 (1C), 129.33 (1C), 128.09 (1C), 127.26 (1C), 127.05 (1C), 125.24 (1C), 123.80 (1C), 123.69 (1C), 123.47 (1C), 122.89 (1C), 122.77 (1C), 121.94 (1C), 121.06 (1C), 120.44 (1C), 115.39 (1C), 44.72 (1C), 44.69 (1C), 36.72 (2C), 32.01 (4C), 31.81 (2C), 30.19 (2C), 29.75 (8C), 29.44 (4C), 26.70 (4C), 22.77 (8C), 14.21 (4C).

HR-MS (Fig. S12): m/z (%): 966.7065 (100) [M+H]⁺ (calcd. C64H92N3O4=966.7088).



Fig. S11. ¹³C NMR spectrum of PDI-NH₂.



Fig. S12. HR-MS spectrum of PDI-NH₂.

Synthesis of H-shaped PDI Gemini (PDI-NH-PDI)



Scheme S3. Preparation of PDI-NH-PDI.

¹H NMR (300 MHz, CDCl₃, **Fig. S13**): δ10.18–9.80 (s, 1H), δ 8.75–8.25 (m, 12H), δ 7.75–7.60 (s, 2H), δ 4.12–3.90 (d, 4H), δ 3.90–3.72 (d, 4H), δ 2.01–1.78 (m, 2H), δ 1.78–1.65 (m, 2H), δ 1.50–0.98 (m, 128H), δ 0.98–0.75 (t, 24H).

¹³C NMR (300 MHz, CDCl₃, **Fig. S14**): δ 163.53 (2C), 163.41 (2C), 163.35 (2C), 162.96 (2C), 147.91 (1C), 142.35 (1C), 135.65 (1C), 134.96 (1C), 134.86 (1C), 134.36 (1C),

133.18 (1C), 131.61 (1C), 131.14 (1C), 130.61 (1C), 130.28 (1C), 130.05 (1C), 129.67 (1C), 128.97 (4C), 128.84 (4C), 128.71 (4C), 128.19 (4C), 126.58 (1C), 125.41 (1C), 123.01 (1C), 122.89 (1C), 122.43 (1C), 122.25 (1C), 121.95 (1C), 121.86 (1C), 117.56 (1C), 116.25 (1C), 113.10 (1C), 44.60 (2C), 44.32 (2C), 36.62 (2C), 36.40 (2C), 31.95 (8C), 31.72 (2C), 31.50 (2C), 30.12 (4C), 29.96 (4C), 29.69 (8C), 29.64 (4C), 29.59 (4C), 29.39 (4C), 29.36 (4C), 29.34 (4C), 26.51 (4C), 26.31 (4C), 22.70 (8C), 14.14 (8C). HR-MS (**Fig. S15**): m/z (%): 1916.3888 (100) $[M+H]^+$ (calcd. C128H18014N415NO8 = 1916.3802).



Fig. S13. ¹H NMR spectrum of PDI-NH-PDI.



Fig. S14. ¹³C NMR spectrum of PDI-NH-PDI.



Fig. S15. HR-MS spectrum of PDI-NH-PDI.



Fig. S16. Photographs of PDI-NH-PDI solutions in CHCl₃ (1 mg mL⁻¹). Under irradiation of visible-light (left) and 365 nm light (right), respectively.



Fig. S17. Three-dimensional (3D) structure of PDI-NH-PDI calculated by Materials Studio.

Supporting figures



Fig. S18. AFM images of irregular aggregates formed by the self-assembly of PDI-NH-PDI in $CHCl_3$ /hexane (1/2 v/v) (a) and $CHCl_3$ /hexane (1/5 v/v) (b). Same results were found for the SD and NP method.



Fig. S19. AFM (a, b and c) and SEM (d, e, f and g) images of the ultralong helices formed by PDI-NH-PDI in CHCl₃/hexane solution (CHCl₃/hexane, 1/15, v/v) via NP. The same results were obtained for CHCl₃/hexane, 1/10, 1/15 and 1/20 (v/v).



Fig. S20. Rectangular nanocrystals of PDI-NH-PDI in CHCl₃/hexane (1/15 v/v) after solvent diffusion for 2 days. AFM image with low-magnification (a) and TEM image with high-magnification (b and c) of the rectangular nanocrystals formed by PDI-NH-PDI in CHCl₃/hexane (1/15 v/v).



Fig. S21. The contour length (a) and thickness (b) distributions of the PDI-NH-PDI assemblies formed in CHCl₃/hexane (1/15 v/v) via SD method, at different aging time indicated in the figures.

Time	$L_{\rm Ave}{}^a$ (µm)	L_{n}^{b} (µm)	$L_{\rm w}^{\ c}$ (µm)	$\mathrm{PDI}_{L^{d}}$	$T_{\rm Ave}^{e}({\rm nm})$	$T_n^f(nm)$	$T_{\rm w}^{g}$ (nm)	PDI _T ^h
2 h	0.82 ± 0.17	0.81	0.85	1.05	9.3 ± 1.6	9.43	9.73	1.03
4 h	0.92 ± 0.16	0.92	0.95	1.03	19.2 ± 2.9	19.24	19.72	1.02
1 day	1.12 ± 0.12	1.11	1.13	1.02	24.9 ± 3.3	24.92	25.34	1.02
2 days	1.11 ± 0.15	1.11	1.14	1.03	23.5 ± 4.5	23.48	24.39	1.04

Table S1. Dimensional data of the rectangular nanocrystals

^{*a*}Average length counted by ImageJ. ^{*b*}Number average length, ^{*c*}Weight average length and ^{*d*}polydispersity index of length calculated based on the counted data. ^{*e*}Average thickness counted by ImageJ. ^{*f*}Number average thickness, ^{*g*}Weight average thickness and ^{*h*}polydispersity index of thickness calculated based on the counted data. The calculations are detailed in page S24.



Fig. S22. Self-assembled nanostructures of PDI-NH-PDI in CHCl₃/hexane (1/20 v/v) after solvent diffusion for 4h. AFM images of the intermediates (fibers) of rectangles. Loosely arranged fibers (a, b and c) and tightly arranged fibers (d, e and f).



Fig. S23. Self-assembled pyramid-shaped parallelogram nanocrystals of PDI-NH-PDI in CHCl₃/hexane (1/20 v/v) after solvent diffusion for 1 day. AFM topography image (a) and phase image (b) of the self-assembled parallelogram sheets. (c) Line profile along the dotted red line in panel (b) shows the thickness of \sim 34 nm for the whole parallelogram sheets as well as the thickness of \sim 2.1 nm for the single layers which are the forming units of parallelogram sheets. Three-dimensional AFM (d) and TEM (e) images of the parallelogram sheets.



Fig. S24. Self-assembled pyramid-shaped parallelogram nanocrystals of PDI-NH-PDI in $CHCl_3$ /hexane (1/20 v/v) after diffusion for 2 day. Three-dimensional AFM (a) and SEM (e) images of pyramid-shaped parallelogram nanocrystals.



Fig. S25. The contour length (i) and thickness (j) distribution of the PDI-NH-PDI assemblies formed in CHCl₃/hexane (1/20 v/v) via SD method, different aging time indicated in the figures.

Time	$L_{\rm Ave}{}^a(\mu{ m m})$	L_{n}^{b} (µm)	$L_{\rm w}{}^c$ (µm)	PDI_L^d	$T_{\rm Ave}^{e}({\rm nm})$	$T_n^f(nm)$	$T_{\mathbf{w}}^{g}$ (nm)	PDI _T ^h
4 h	2.15 ± 0.51	2.16	2.28	1.06	6.3 ± 0.5	6.30	6.34	1.01
1 day	2.95 ± 0.36	2.94	2.98	1.01	34.8 ± 2.7	34.74	34.95	1.01
2 days	2.95 ± 0.31	2.95	2.98	1.01	42.0 ± 3.3	41.91	42.17	1.01

Table S2. Dimensional data of the pyramid-shaped parallelogram nanocrystals

^{*a*}Average length counted by ImageJ. ^{*b*}Number average length, ^{*c*}Weight average length and ^{*d*}polydispersity index of length calculated based on the counted data. ^{*e*}Average length counted by ImageJ. ^{*f*}Number average length, ^{*g*}Weight average length and ^{*h*}polydispersity index of thickness calculated based on the counted data. The calculation is detailed in Supplementary page 24-25.



Fig. S26. Self-assembled pyramid-shaped rectangles of PDI-NH-PDI in CH_2Cl_2 /hexane (1/15 v/v) after diffusion for 2 days. AFM topography image (a), phase image (b,c) and three-dimensional image (d) of the self-assemblies.



Fig. S27. AFM topography image of the self-assembled pyramid-shaped micro-sheets of PDI-NH-PDI in THF/hexane (1/15 v/v) after diffusion for 2 days. It can be concluded that change good solvent may change aspect ratio of the self-assemblies.



Fig. S28. Self-assembled micro-sheets of PDI-NH-PDI in $CHCl_3/Methanol (1/15 v/v)$ after diffusion for 2 days. AFM topography images (a and b) and SEM image (c) of the self-assembled sheets. The thickness of the single layer forming the ultimate thicker sheets is $2.2 \sim 2.3$ nm. It can be concluded that more polar selective-solvents are not benefit for self-assembly of PDI-NH-PDI, it tends to form irregular assemblies.



Fig. S29. Self-assembled uniform nanospheres of PDI-NH-PDI in $CHCl_3$ /acetonitrile (1/15 v/v) after diffusion for 2 days. AFM topography image (a) and SEM images (c and d) of the self-assembled nanoparticles.

Supplementary calculation

Determination of statistical data of the assemblies' dimensions. Dimension (length, thickness, diameter and pitch) distributions the assemblies (rectangle, parallelogram and helix) were counted via the software ImageJ of the National Institutes of Health. ~ 200 assemblies were traced via ImageJ to obtain the length, thickness, diameter and pitch information. The number average rectangle/parallelogram length (L_n), weight average rectangle/parallelogram thickness (T_n), weight average rectangle/parallelogram thickness (T_w), number average helix

diameter (D_n), weight average helix diameter (D_w), number average helix pitch (P_n) and weight average helix diameter (P_w) were calculated according to below equations⁴:

$$L_{n} = \frac{\sum_{i=1}^{n} N_{i}L_{i}}{\sum_{i=1}^{n} N_{i}} \qquad L_{w} = \frac{\sum_{i=1}^{n} N_{i}L_{i}^{2}}{\sum_{i=1}^{n} N_{i}L_{i}}$$

$$T_{n} = \frac{\sum_{i=1}^{n} N_{i}T_{i}}{\sum_{i=1}^{n} N_{i}} \qquad (2) \qquad T_{w} = \frac{\sum_{i=1}^{n} N_{i}T_{i}^{2}}{\sum_{i=1}^{n} N_{i}T_{i}}$$

$$D_{n} = \frac{\sum_{i=1}^{n} N_{i}D_{i}}{\sum_{i=1}^{n} N_{i}} \qquad (4) \qquad D_{w} = \frac{\sum_{i=1}^{n} N_{i}D_{i}^{2}}{\sum_{i=1}^{n} N_{i}D_{i}}$$

$$(5) \qquad P_{n} = \frac{\sum_{i=1}^{n} N_{i}P_{i}}{\sum_{i=1}^{n} N_{i}} \qquad (6) \qquad P_{w} = \frac{\sum_{i=1}^{n} N_{i}P_{i}^{2}}{\sum_{i=1}^{n} N_{i}P_{i}}$$

$$(7) \qquad (8) \qquad P_{w} = \frac{\sum_{i=1}^{n} N_{i}P_{i}}{\sum_{i=1}^{n} N_{i}P_{i}}$$

where L and T are the length and thickness of rectangle or parallelogram, respectively. D and P refer to the diameter and pitch of the helix, respectively. N denotes the number of the corresponding assemblies.

Calculate the *d*-spacing parameters of lattice planes via selected area electron diffraction (SAED). Firstly, draw a parallelogram using red dashed lines via the "insert line" instruction in word, which was formed by the central spot and three different adjacent spots around the central spot, as shown in Fig. S30 and S31. O, R_1 , R_2 and R_3 were indicated in the corresponding locations. Secondly, the parameters of the lattice

planes, l_1 , l_2 and l_3 , were measured via the software ImageJ of the National Institutes of Health. The corresponding *d*-spacings (d_1 , d_2 and d_3) are calculated according to below equation:

(9)
$$d_n = \frac{1}{l_n}$$

The *d*-spacing parameters of lattice planes of rectangle and parallelogram assemblies were listed in Table S1 and Table S2, respectively.



Fig. S30. SAED pattern of the rectangular nanocrystals formed by PDI-NH-PDI in CHCl₃/hexane (1/15 v/v). O, R₁, R₂ and R₃ as well as the corresponding parallelogram formed by the four spots were indicated in the corresponding locations.

	Table S3. Para	meters of lattic	ce planes of r	ectangular n	anocrystals	5
<i>l</i> ₁ (1/nm)	<i>l</i> ₂ (1/nm)	<i>l</i> ₃ (1/nm)	<i>d</i> ₁ (nm)	<i>d</i> ₂ (nm)	<i>d</i> ₃ (nm)	d _{mean} (nm)
2.135	2.181	2.120	0.468	0.458	0.472	0.466



Fig. S31. SAED pattern of the pyramid-shaped parallelogram nanocrystals formed by PDI-NH-PDI in CHCl₃/hexane (1/20 v/v). O, R₁, R₂ and R₃ as well as the corresponding parallelogram were indicated in the corresponding locations.

Table S4. Parameters of lattice planes of pyramid-shaped parallelogram nanocrystals.							
<i>l</i> ₁ (1/nm)	<i>l</i> ₂ (1/nm)	<i>l</i> ₃ (1/nm)	<i>d</i> ₁ (nm)	<i>d</i> ₂ (nm)	<i>d</i> ₃ (nm)	d _{mean} (nm)	
2.050	2.100	2.037	0.488	0.476	0.491	0.485	

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