Supporting information for

Hierarchical Structures Formed from Self-Complementary Sextuple Hydrogen-Bonding Arrays

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Experimental Section

Materials

2,6-Diaminopyridine (2,6-DAP) was purchased from Aldrich (USA) and recrystallized from chloroform. All other chemicals were purchased from Aldrich (USA) or Acros Organics (Germany) and were used as received. All solvents were purchased from TEDIA (USA) and distilled over CaH_2 prior to use.

Characterizations

FT-IR spectra were obtained from Nicolet Avatar 320 FT-IR spectrometer; 32 scans were collected with a spectral resolution of 1 cm^{-1}.The conventional KBr disk method was employed. Sample was dissolved in DMF and then cast onto a KBr disk and dried in vacuum at 120 °C for 24 h.

Nuclear Magnetic Resonance (NMR) measurement. ^{1}H-NMR spectra were recorded using a Varian Inova- 500 MHz spectrometer equipped with a 9.395 T Bruker magnet. Samples of ca. 5 mg were analyzed at 25 °C in deuterated solvent. ^{13}C-NMR spectra were performed on a Varian Inova- 500 MHz spectrometer operated at 125 MHz. All samples of ca. 20 mg were dissolved in deuterate solvent and analyzed at 25 °C

Elemental Analysis (EA). The carbon, hydrogen, and nitrogen atom contents of the samples were obtained using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany).

Gas Chromatography/Mass Spectrometry. GC/MS spectra were acquired using a Micromass Trio 2000 mass spectrometer (Micromass, Beverly, MA).

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy. MALDI-TOF MS was performed using a Model Bruker AutoFlex equipped with a 337-nm N_2 laser (over 20 Hz).

Differential Scanning Calorimetry (DSC). DSC was performed using a TA DSC-Q20 controller operated under a dry nitrogen atmosphere. The samples were weighed (ca. 5–10 mg), sealed in an aluminum pan, and then heated from –90 to +300 °C at a rate of 10 °C/min.

Wide-Angle X-ray Diffraction (WAXD). WAXD patterns of powders were obtained using a Rigaku D/max-2500 X-ray diffractometer. The radiation source was Ni-filtered Cu Kα radiation at a wavelength of 0.154 nm. The voltage and current were set at 30 kV and 20 mA, respectively. The sample was mounted on a circular sample holder; the data were collected by a proportional counter detector over the 2d range from 2 to 50° at a rate of 5° min^{-1}. Bragg's law ($\lambda = 2d \sin\theta$) was used to compute the d-spacing corresponding to the complementary behavior.

Wide Angle X-ray Scattering (WAXS). WAXS was collected by the 01C2 SWLS beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. For the experiment, radiation with a wavelength of 0.103316 nm was used. The beam size possessed diameter of 100 mm at the sample position, which was defined by a pinhole collimator. All tests were performed at ambient conditions (23 °C, 65% relative humidity).

Molecular Dynamic Simulation. The modelling work presented here was performed using ChemOffice 2008. The structure of U-DPy were drawn initially by ChemDraw. Each 2D structure was converted into 3D structure by Chem3D, followed by molecular mechanics minimization using MM2 force field. MM2 parameters used here are the "MM2 (1991) Parameter Set" provided by N. L. Allinger, (University of Georgia) and implemented in Chem3D. Molecular simulation was used to model the *d* spacing of a molecule and the calculated results were evaluated in comparison with experimental data.

UV–Vis and Photoluminescence (PL) Spectra. UV–Vis and photoluminescence (PL) spectra were measured using an HP 8453 diode-array spectrophotometer and a Hitachi F-4500 luminescence spectrometer, respectively. All samples were excited at 345 nm, the absorbance maxima for pyrene. The fluorescence titration was performed as the procedures described previously.[1]

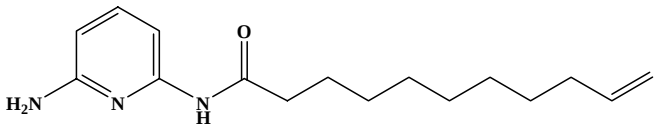
Scanning Electron Microscopy (SEM) images were obtained using a JEOL-7401F field emission (FE) SEM microscope operated at 15 kV. The sample for SEM investigation was prepared by placing a drop of the sample solution onto a glass substrate and then evaporating the solvent (toluene).

Transmission Electron Microscopy (TEM) images were obtained by FEG-TEM instrument operated at 100 kV. To prepare samples for TEM, a dilute solution of sample in toluene was placed on a carbon-coated copper grid and stained by RuO_4.

Atomic Force Microscopy (AFM). Height measurements of the microcapsules were determined using tapping-mode AFM (Digital Instrument NS4/D3100CL/Multi- Mode AFM; Veeco-Digital Instruments, Santa Barbara, CA) with silicon cantilevers (Pointprobe Silicon AFM Probe) at 25 °C in air. The samples preparation was the same as for SEM procedure.

Syntheses

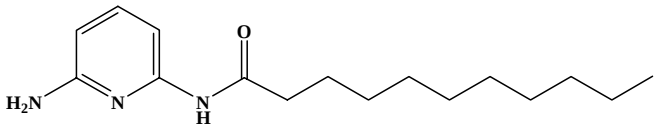
***N*-(6-Aminopyridin-2-yl)undec-10-enamide (1)**.



(1)

2,6-Diaminopyridine (24.0 g, 215 mmol, 500 mol%) and triethylamine (8.70 g, 86 mmol, 200 mol%) were dissolved in dry THF (100 mL) and cooled to 0 °C in an ice bath. A solution of 10-undecenoyl chloride (8.72 g, 43 mmol, 100 mol%) in dry THF (40 mL) was added dropwise over a period of 1.5 h and the reaction mixture was stirred at 0 °C for 3 h, then maintained at 25 °C for an additional 12 h. Finally, the mixture was filtered, the solvent was evaporated, and the residue was purified through chromatography (SiO_2; 20% *n*-hexane/ethyl acetate) to obtain the product (a yellow viscous oil). (10.94 g, yield = 92%). Tg: – 40 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.88 (s, 1H; NH), 7.49 (d, 1H; PyH), δ = 7.39 (t, PyH), 6.20 (d, 1H; PyH), 5.83–5.68 (m, 1H; CH), 4.90 (dd, 2H; CH_2), 4.29 (br, 2H; NH_2), 2.40 (t, 2H; CH_2), 2.05–1.88 (m, 2H; CH_2), 1.77–1.54 (m, 2H; CH_2), 1.49–1.20 (m, 13H; CH_2, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 171.8, 157.3, 150.0, 140.4, 139.48, 114.3, 104.3, 103.5, 38.0, 33.9, 29.5, 29.4, 29.2, 29,1, 25.6 ppm; MS (EI): *m*/*z* 275 $[M]^+$; EA: calcd (%) for $C_{16}H_{25}N_3O$: C, 69.78; H, 9.15; N, 15.26; O, 5.81. Found: C, 69.74; H, 9.11; N, 14.98; O, 6.17.

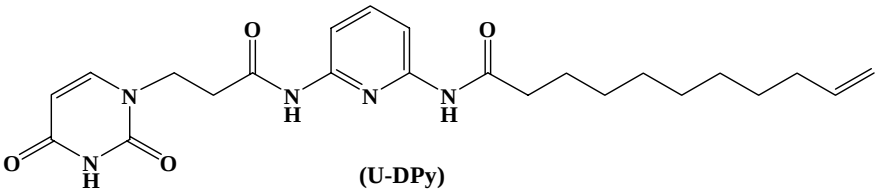
***N*-(6-aminopyridin-2-yl)undecanamide (2).**



(2)

This compound was prepared as described in compound1 except the use of replacing by undecanoyl chloride (10.2 g, 50 mmol, 100 mol%). The product was isolated by column chromatography using silica gel and 30% *n*-hexane/ethyl acetate as eluents to give a yellow viscous oil of 11.44 g and yield = 82%. M.p.: -23 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93 (s, 1H; NH), 7.52 (d, 1H; PyH), δ = 7.39 (t, PyH), 6.20 (d, 1H; PyH), 4.35 (br, 2H; NH_2), 2.37 (t, 2H; CH_2), 1.74–1.54 (m, 2H; CH_2), 1.39–1.15 (m, 14H; CH_2), 0.83 (t, 3H; CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 171.9, 157.3, 150.1, 140.3., 114.3, 104.3, 103.6, 37.9, 32.0, 29.7, 29.6, 29.5, 29.4, 29.4, 25.6, 22,8, 14.3 ppm; MS (EI): *m*/*z* 277 $[M]^+$; EA: calcd (%) for $C_{16}H_{27}N_3O$: C, 69.27; H, 9.81; N, 15.15; O, 5.77. Found: C, 69.27; H, 9.81; N, 15.15; O, 6.30.

***N*-(6-(3-(2,4-dioxo-3,4-dihydropyrimidin-1(*2H*)-yl)propanamido)pyridin-2-yl)undec-10-enamide (U-DPy).**



(U-DPy)

Compound (1) (1.00 g, 3.63 mmol, 100 mol%) and triethylamine (0.55 g, 5.4 mmol, 150 mol%) were dissolved in dry THF (40 mL) cooled to 0 °C in an ice bath. A solution of acryloyl chloride (0.40 g, 4.4 mmol, 120 mol%) in dry THF (15 mL) was added dropwise through syringe over a period of 1 h and the reaction mixture was stirred at 0 °C for 2 h and then maintained at 25 °C for an additional 6 h. After evaporating the solvent, the residue was subjected to chromatography (SiO_2; THF) and then the evaporation of THF yielded a brown wax (3), yield = 85% (1.02 g). Compound (3) (1.02 g) was directly added under an argon atmosphere to round-bottomed flask. Then, uracil (4.1 g, ,1000 mol%), potassium *tert*-butoxide (0.05g), and 50 mL of dry DMSO were added at 25 °C. The reaction mixture was heated to 60 °C and the reaction was allowed to proceed for 36 h. The DMSO was removed at 50 °C under vacuum and the product was re-dissolved in chloroform (150ml) with vigorous stir for 3 h and the insoluble solids were removed by filtration. After evaporation of chloroform, the product was purified by recrystallization from acetone, yield: 1.20 g (80%). M.p.: 213 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 12.73 (s, 1H; NH), δ = 10.42 (s, 1H; NH), 10.33 (s, 1H; NH), 8.01 (d, 1H; PyH), 7.74 (t, PyH), 7.67 (d, 1H; PyH), 7.50 (d, 1H; CH), 5.83–5.68 (m, 1H; CH), 5.67 (d, 1H; CH), 4.90 (dd, 2H; CH_2), δ = 7.74 (t, PyH), 4.15 (t, 2H; CH_2), 3.12 (t, 2H; CH_2), 2.43 (t, 2H; CH_2), 1.96 (m, 2H; CH_2), 1.65 (m, 2H; CH_2),1.53–1.07 (m, 10H; CH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 173.8, 169.3, 165.7,153.1, 151.5, 149.55, 147.6, 141.1, 139.5, 114.3, 111.7, 110.7, 102.3, 46.3, 37.0, 34. 0, 33.7, 29.7, 29.6, 29.5, 29.4, 29.4, 25.6 ppm; FAB MS: m/z: 442 $[M+H]^+$; EA: calcd (%) for $C_{23}H_{31}N_5O_4$: C, 62.57; H, 7.08; N, 15.86; O, 14.49. Found: C, 62.23; H, 7.04; N, 15.42; O, 15.31.

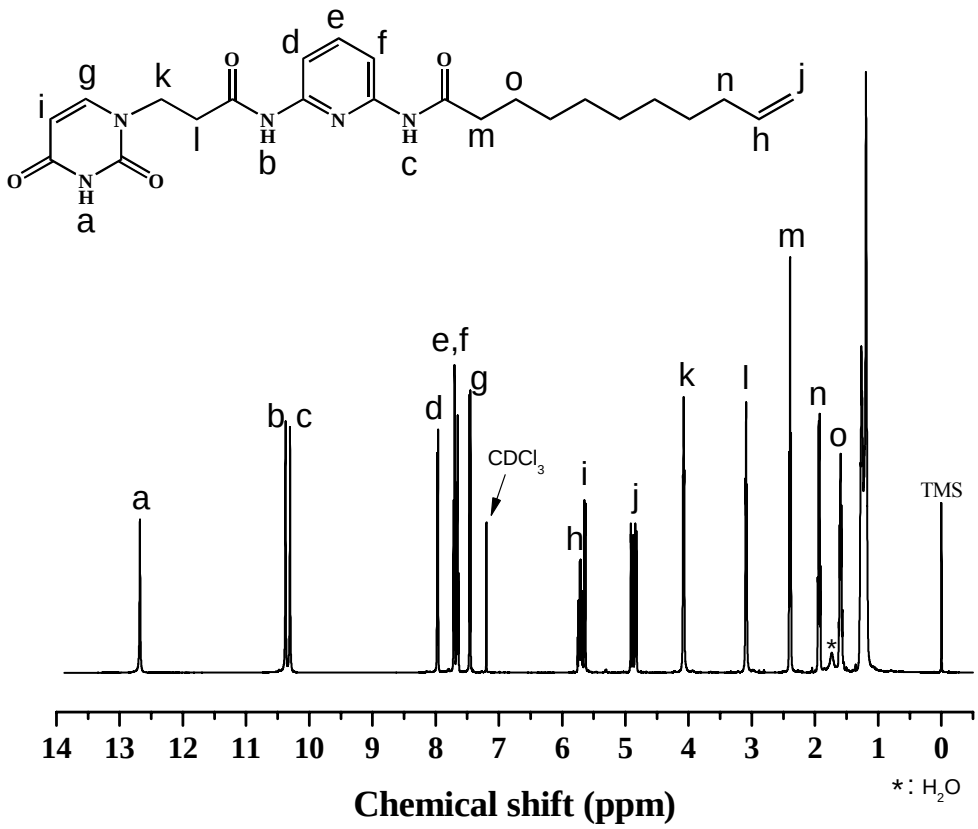


Figure S1: ^{1}H-NMR spectrum of U-DPy in $CDCl_3$.

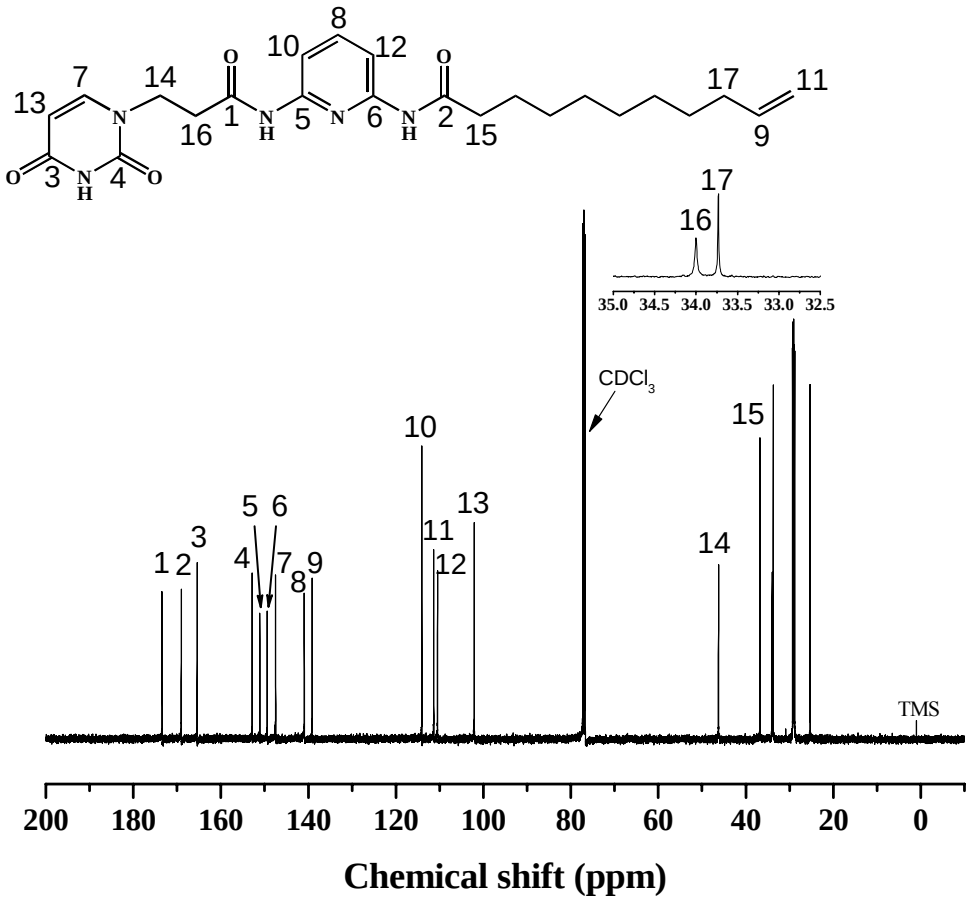


Figure S2: ^{13}H-NMR spectrum of U-DPy in $CDCl_3$.

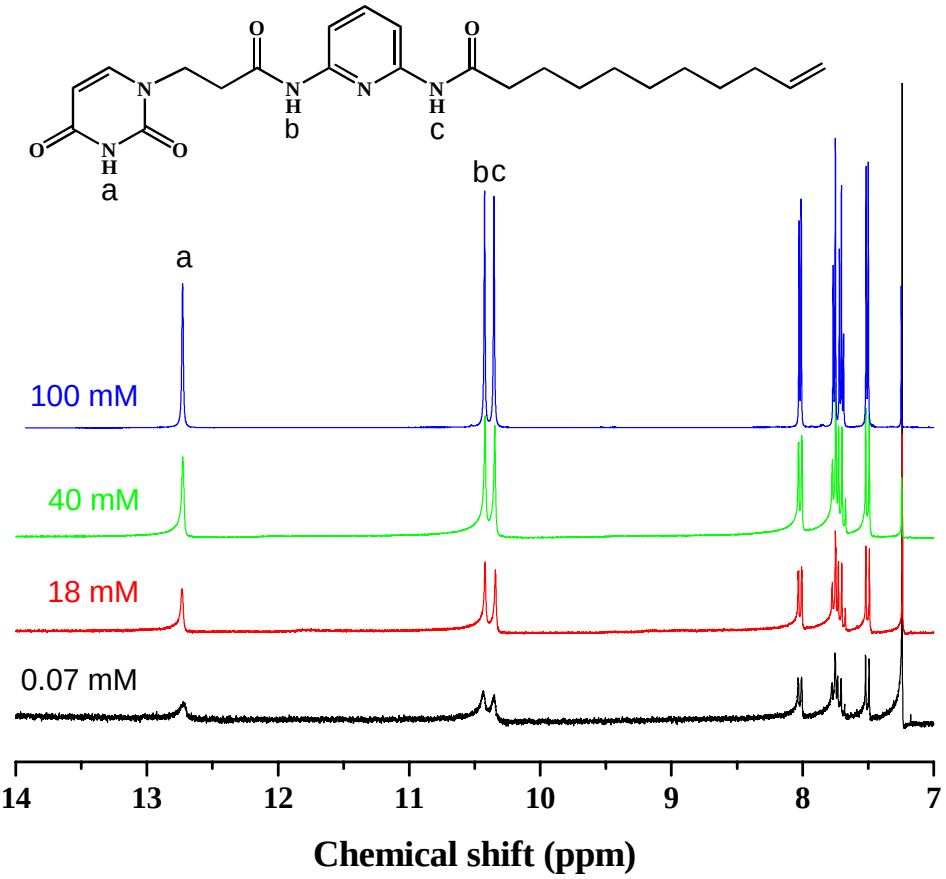
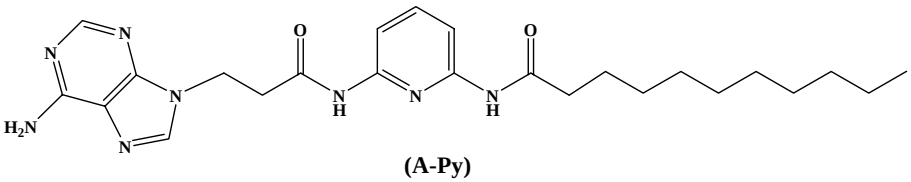


Figure S3: ^{1}H-NMR spectrum of U-DPy in the presence of various amounts of $CDCl_3$.

***N*-(6-(3-(6-amino-9H-purin-9-yl)propanamido)pyridin-2-yl)undecanamide (A-Py).**



(A-Py)

The preparation of the adenine derivatives was prepared by similar procedure to that described for U-DPy using compound 2 (0.50 g, 1.81 mmol, 100 mol%) instead of compound 1, yield: 0.71 g (84%). M.p.: 190 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): 8.31 (s, 1H; NH), 7.92 (d, 2H; PyH), 7.90 (s, 1H; CH), 7.79 (br, 1H; NH), 7.65 (t, PyH), 7.61 (br, 1H; NH), 5.67 (s, 1H; NH2), 4.57 (t, 2H; CH_2), 2.99 (t, 2H; CH_2), 2.32 (t, 2H; CH_2), 1.74–1.54 (m, 2H; CH_2), 1.42–1.00 (m, 14H; CH_2), 0.84 (t, 3H; CH_3) ppm; ^{13}C NMR (125 MHz, d6-DMSO, 25 °C): δ = 172.8, 170.2, 156.6, 153.0, 151.1, 150.5, 1503, 150.1, 141.7, 140.4, 119.4, 109.7, 40.8, 36.6, 36.3, 32.1, 29.6, 29.5, 29.4, 29.3, 29.3, 25.6, 22,8, 14.7 ppm; MS (EI): *m*/*z* 466 $[M]^+$; EA: calcd (%) for $C_{24}H_{34}N_8O_2$, 61.78; H, 7.34; N, 24.02; O, 6.86. Found: C, 61.27; H, 7.28; N, 24.44; O, 7.01.

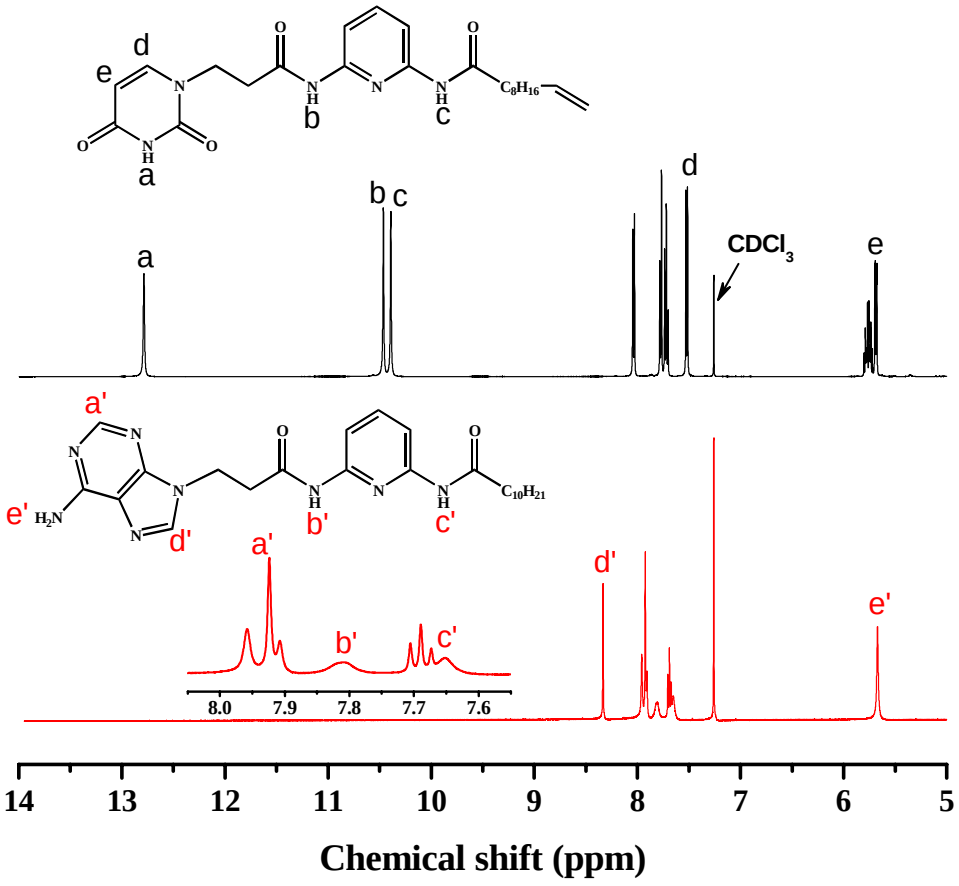
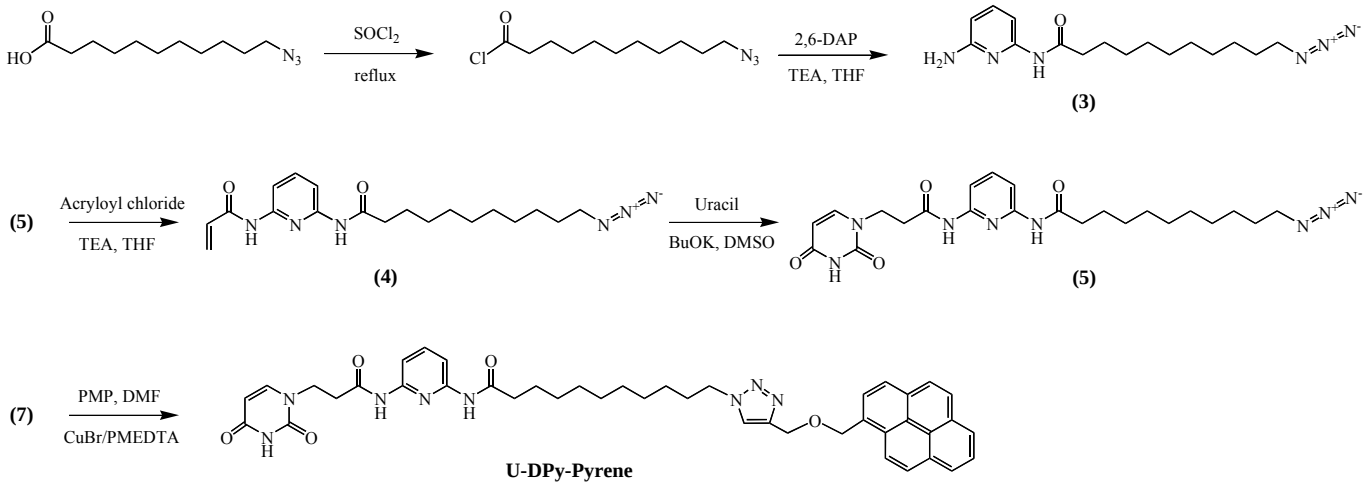


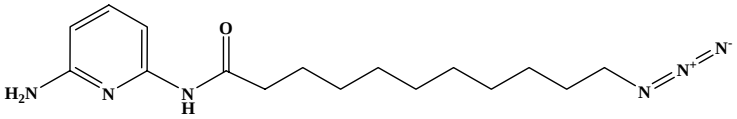
Figure S4: Comparison of ^{1}H-NMR spectra between U-DPy and A-DPy in $CDCl_3$.

Synthesis of pyrene-based U-DPy via click reaction.



Here we present the synthesis of a novel U-DPy-Pyrene**,** which was obtained in five steps including click chemistry with high overall yield of 83 %. Because "click" cycloaddition can be performed under very mild conditions, and conducted in high yields, and little or no side reactions.[2-4]

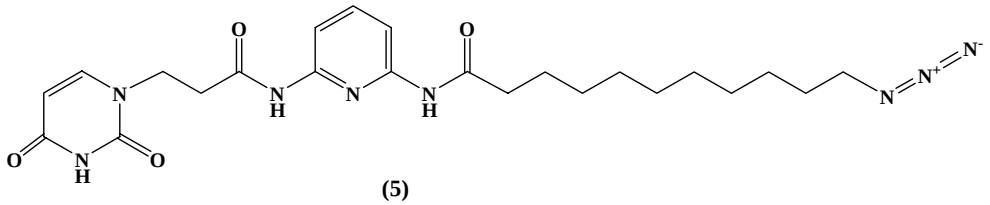
***N*-(6-aminopyridin-2-yl)-11-azidoundecanamide (3)**



(3)

11-azidoundecanoic acid was synthesized from commercial 11-bromoundecanoic acid according to the procedures described previously.[5] 11-azidoundecanoic acid (1.00 g, 4.4 mmol, 100 mol%) was first treated with an excess of thionyl chloride (5 mL, 68.0 mmol) and refluxed for 6 h, then 11-azidoundecanoyl chloride (1.1 g) was obtained by evaporating the thionyl chloride and dried under vacuum. 2,6-Diaminopyridine (2.88 g, 26.4 mmol, 600mol%) and triethylamine (0.89 g, 8.8 mmol, 200 mol%) were dissolved in dry THF (40 mL) cooled to 0 °C in an ice bath. A solution of 11-azidoundecanoyl chloride in dry THF (15 mL) was added dropwise through syringe over a period of 1.5 h and the reaction mixture was stirred at 0 °C for 3 h and then maintained at room temperature for an additional 12 h. After evaporating the solvent, the residue was subjected to chromatography (SiO_2; 30% *n*-hexane/ethyl acetate) and then the product was dried under vacuum, yield: 80% (1.12 g); M.p.: 56 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.59 (s, 1H; NH), 7.52 (d, 1H; PyH), 7.41 (t, PyH), 6.21 (d, 1H; PyH), 4.27 (br, 1H; NH_2), δ = 3.20 (t, CH_2), 2.30 (t, 2H; CH_2), 1.67 (m, 2H; CH_2), 1.56 (t, 2H; CH_2), 1.48–1.00 (m, 12H; CH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 171.8, 157.3, 150.0,140.3, 104.4, 103.4, 51.6, 38.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 26.8, 25.6 ppm; MS (EI): *m*/*z* 318 $[M]^+$; EA: calcd (%) for $C_{16}H_{26}N_6O$: C, 60.35; H, 8.23; N, 26.39; O, 5.02. Found: C, 60.08; H, 8.19; N, 26.09; O, 5.64.

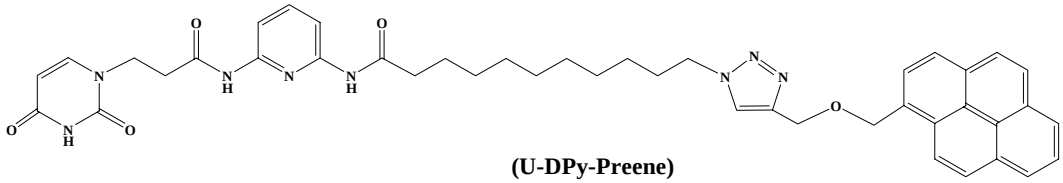
11-azido-*N*-(6-(3-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)propanamido)pyridin-2-yl)undecanamide (5)



(5)

The preparation of the uracil derivatives was prepared by similar procedure to that of U-DPy except the use of which instead by compound 3 (1.0 g, 3.14 mmol, 100 mol%). Finally, the product was purified by recrystallization from acetone, yield: 1.14 g (74%). M.p.: 201 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 12.70 (s, 1H; NH), 10.36 (s, 1H; NH), 10.30 (s, 1H; NH), 7.97 (d, 1H; PyH), 7.73 (t, PyH), 7.65 (d, 1H; PyH), 7.48 (d, 1H; CH), 5.64 (d, 1H; CH), 4.09 (t, 2H,CH_2), 3.18 (t, 2H,CH_2), 3.09 (t, 2H, CH_2), 2.32 (t, 2H; CH_2), 1.59 (m, 2H; CH_2), 1.50 (t, 2H; CH_2), 1.40–0.90 (m, 12H; CH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 173.6, 169.3, 165.7, 153.1, 151.3, 149.6, 147.6, 141.1, 111.6, 110.7, 102.3, 51.6, 46.5, 36.9, 34.2, 29.7, 29.5, 29.4, 29.3, 29.2, 29.0, 26.9, 25.5 ppm; FAB MS: m/z: 485 $[M+H]^+$; EA: calcd (%) for $C_{23}H_{32}N_8O_4$: C, 57.01; H, 6.66; N, 23.13; O, 13.21. Found: C, 57.01; H, 6.62; N, 22.78; O, 13.59.

***N*-(6-(3-(2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)propanamido)pyridin-2-yl)-11-(4-((pyren-1-ylmethoxy)methyl)-1*H*-1,2,3-triazol-1-yl)undecanamide (U-DPy-Preene)**



(U-DPy-Preene)

1-((prop-2-ynyloxy)methyl)pyrene was synthesized from 1-pyrenemethanol and propargyl bromide as previously described.[6] 1-((prop-2-ynyloxy)methyl)pyrene (0.25 g, 0.93 mmol) and compound (7) (0.34 g, 0.71 mmol) were dissolved in DMF (3 mL) and then the resulted solution was purged with a dry argon atmosphere for 10 min. N,N′,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA; 35.3 μL, 0.014 mmol) was added via syringe, leading the mixture to becoming homogeneous and then the solution was degassed through three freeze/thaw evacuation cycles. Upon the addition of CuBr (0.002 mg, 0.02 mmol), the color of the solution was gradually changed from light blue to light green. The solution was heated to 50 °C with stirring under an argon atmosphere until the azide peak (2092 cm^{-1}) completely disappeared (1.5h) as observed through the FTIR spectrum. After cooling to 25 °C, the reaction mixture was passed through an aluminum oxide column to remove the Cu(II) catalyst. Finally, the solvent was evaporated, and the residue was purified by precipitation into acetone; it was then filtrated and dried under vacuum. yield: 0.51 g (95%). M.p.: 161 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 12.55 (s, 1H; NH), 10.29 (s, 1H; NH), 10.25 (s, 1H; NH), 8.40-7.90 (m, 9H, PyreneH), 7.97 (d, 1H; PyH), 7.75 (t, PyH), 7.70 (d, 1H; PyH),

7.45 (d, 1H; CH), 7.43 (s, 1H, triazoleH), 5.62 (d, 1H; CH), 5.28 (s, 1H, CH_2), 4.79 (s, 1H, CH_2), 4.25 (t, 2H, CH_2), 4.05 (t, 2H, CH_2), 3.09 (t, 2H, CH_2), 2.44 (t, 2H; CH_2), 1.78 (m, 2H; CH_2), 1.65 (t, 2H; CH_2), 1.40–1.00 (m, 12H; CH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 173.6, 169.3, 165.7, 152.9, 151.3, 149.6, 147.6, 145.3, 141.1, 131.5, 131.4, 131.1, 130.9, 129.6, 127.9, 127.6, 127.5, 127.4, 126.1, 125.4, 125.1, 124.8, 124.7, 123.6, 122.6, 111.6, 110.7, 102.2, 71.2, 63.9, 50.5, 46.5, 36.9, 34.2, 30.2, 29.5, 29.4, 29.3, 29.2, 29.1, 26.8, 25.5 ppm; MALDI-TOF: *m/z* 755.40 $[M+H]^+$; EA: calcd (%) for $C_{43}H_{46}N_8O_5$: C, 68.42; H, 6.14; N, 14.84; O, 10.60. Found: C, 67.95; H, 6.31; N, 14.54; O, 11.2.

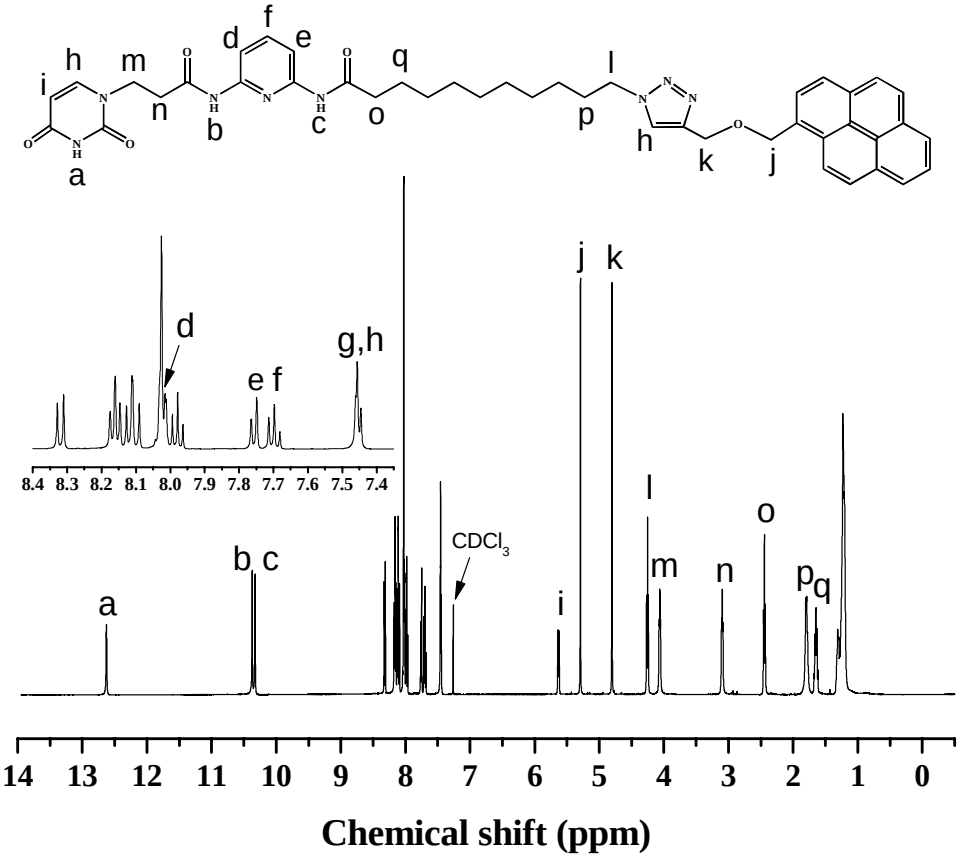


Figure S5: ^1H-NMR spectrum of U-DPy-Pyrene in $CDCl_3$.

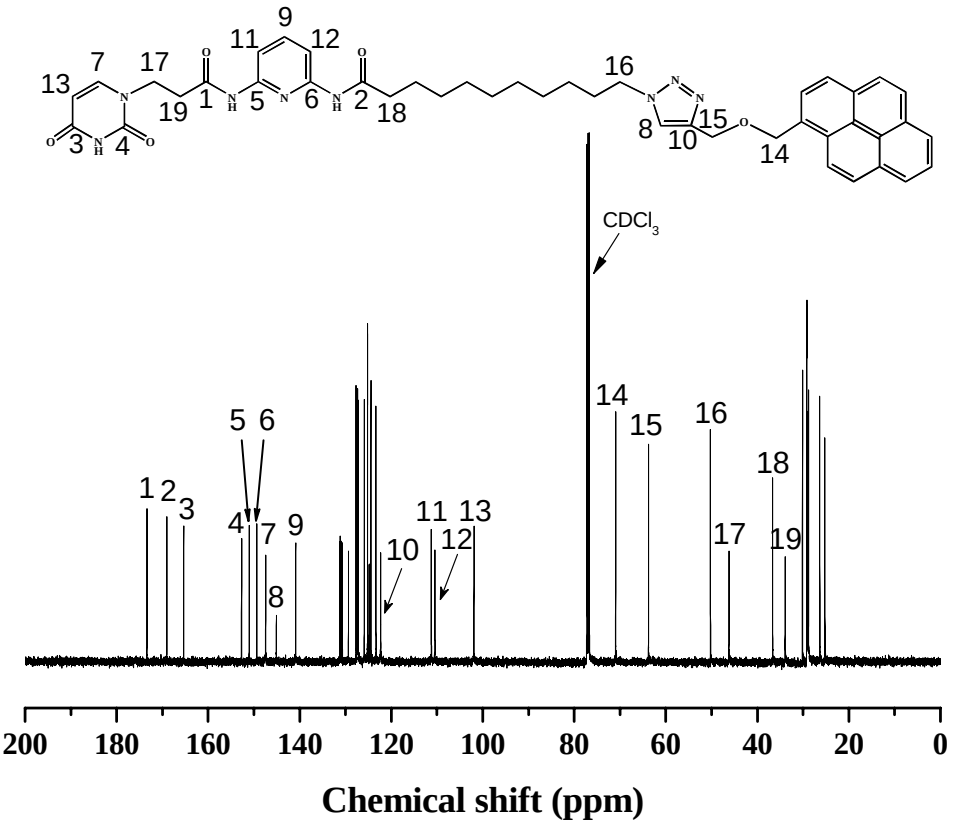
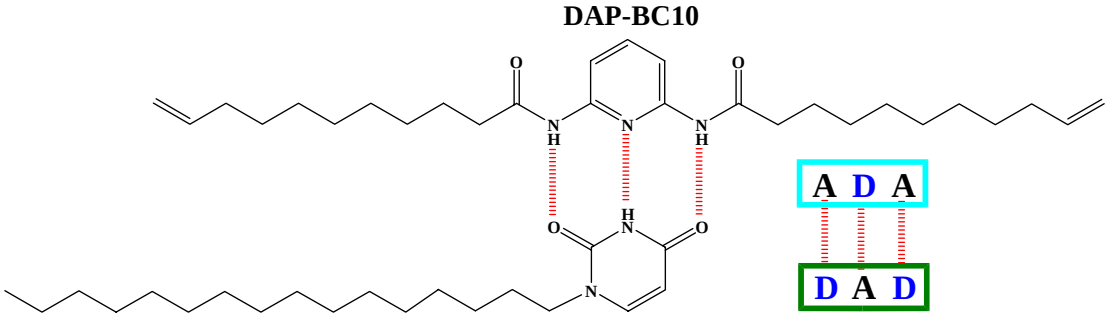


Figure S6: ^{13}H-NMR spectrum of U-DPy-Pyrene in $CDCl_3$.

Variable temperature ^{1}H NMR experiments

Scheme: Structures and schematic representation of the triple hydrogen bonding interaction between microstructures of T-C16 and DAP-BC10.



1-Hexadecyluracil (U-C16) and *N*,*N*'-2,6-Pyridinediylbisundec-10,10'-enamide (DAP-BC10) were synthesized through alkylated nucleobases and amidization, respectively, according to the procedures described previouslypectively.[7,8] For the multiple hydrogen bonded system, DAP is well known that it possess DAD-ADA triple hydrogen-bond arrays with uracil (or thymine).[9] in addition, several important motifs have been reported that the DAP/uracil complex has an association constant of 800 M^{-1} representing a highly co-operative assembly. [10]

U-C16/DAP-B10 Complexes

Desired amounts of U-C16 and DAP-B10 (50:50 molar ratios) were dissolved in toluene-d_8 stirred continuously for 24 h at 25 °C.

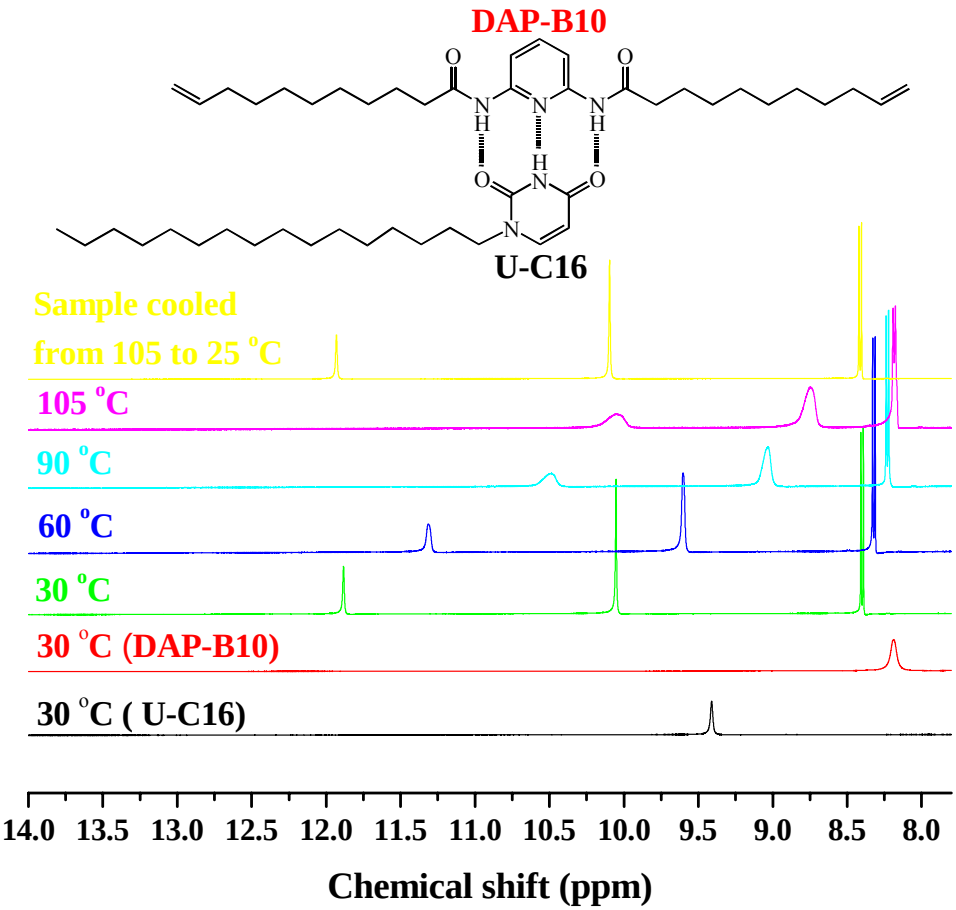


Figure S7: ^{1}H NMR spectra at various temperatures for a 40 mM solution of U-C16/ DAP-B10 complexes in **toluene-d_8**

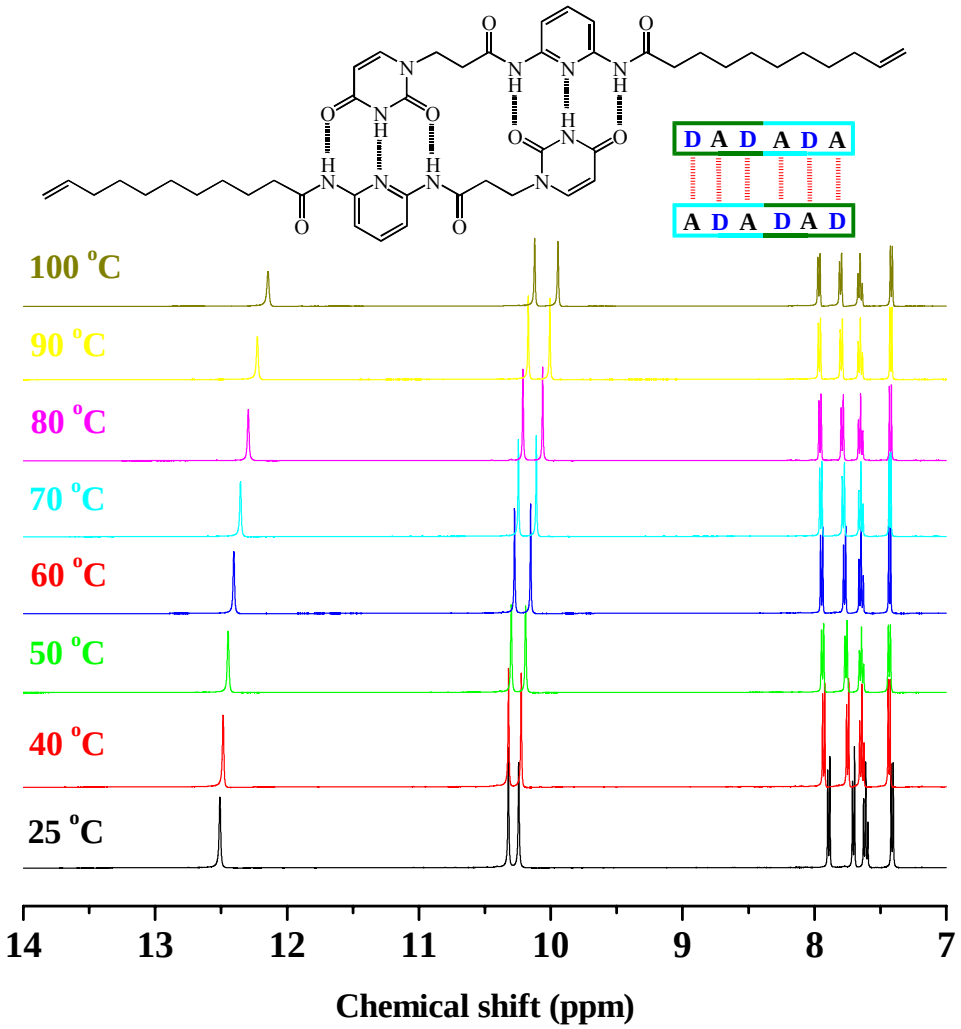


Figure S8a: ^{1}H NMR spectra at various temperatures for a 40 mM solution of U-DPy in **tetrachloroethane-d_2**.

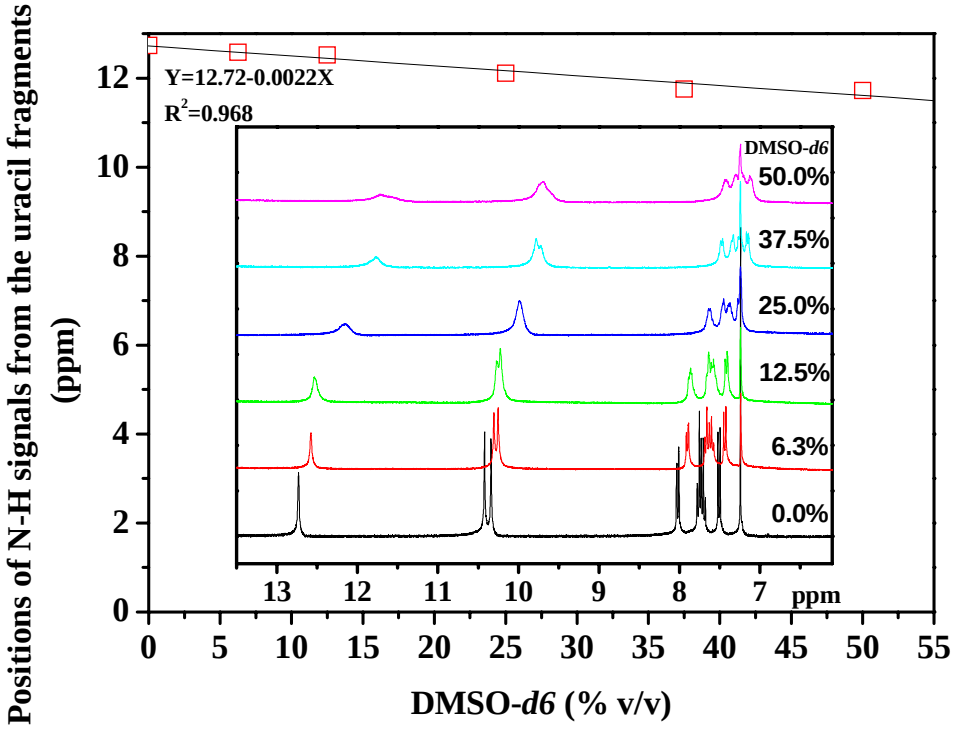


Figure S8b: Dependence o of the amide proton of U-DPy on the concentration of DMSO-*d*6 in CDCl3/DMSO-*d*6 mixtures. The inset displays the corresponding ^{1}H-NMR traces.

Further studies in $CDCl_3$/DMSO-d_6 mixtures were undertaken in order to compare dimerization constants of U-DPy at room temperature, the peak of amide proton was slightly upfield shifted from 12.73 (in pure $CDCl_3$) to 11.72 ppm (in $CDCl_3$ containing 50% DMSO-d_6) (Figure S8b). The results presented in Figure S8b suggest that U-DPy formed highly stable hydrogen-bonded complexes at high concentrations of DMSO-d_6 (50%). From the linear dependence of [the amide proton of uracil] vs [DMSO-*d*6 (% v/v)], a slop of -0.0022 (R^2 = 0.968) was predicted for pure $CDCl_3$.

Fluorescence titration

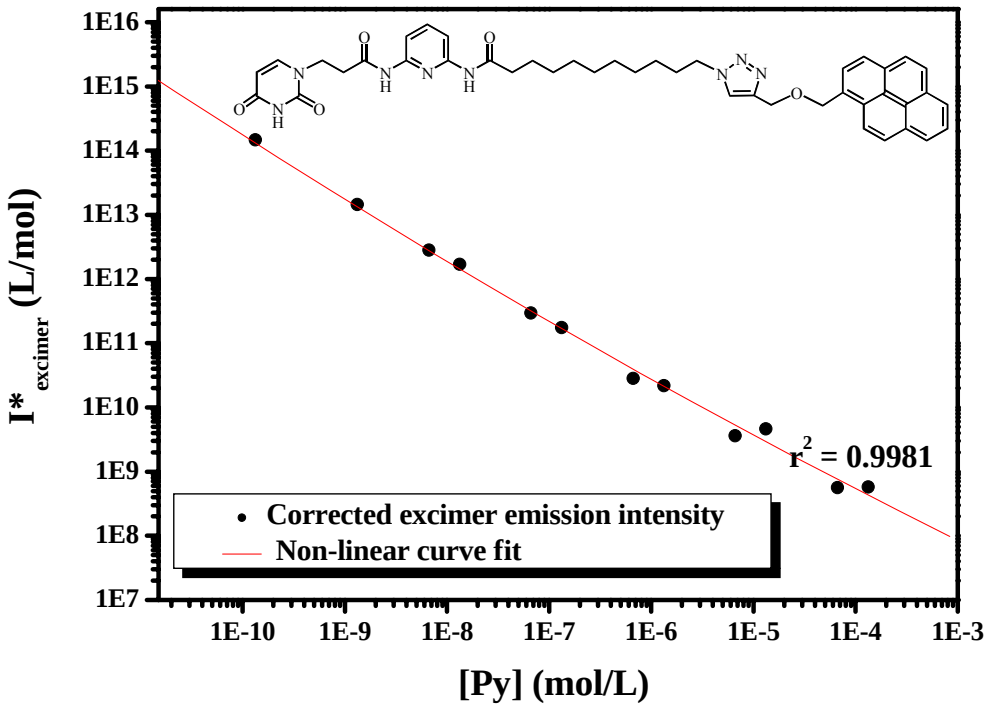


Figure S9: Plot of I* excimer vs. concentration, showing non-linear curve fit and calculated K_{dimer} for U-DPy-Pyrene in chloroform.

Diffusion Ordered Spectroscopy (DOSY) NMR experiments

DOSY experiments provide a way to separate the different compounds in a mixture based on the differing translation diffusion coefficients and therefore differences in the size. Further studies were undertaken in order to compare diffusion coefficients of U-DPy at room temperature, as the monomer concentration is increased from 10.7 to 107 mg/dL in $CDCl_3$, the measured weight-average diffusion coefficients were almost unchanged from 2.15×10^{-10} to 2.45×10^{-10} $m^2 s^{-1}$, indicating that the U-DPy form highly stable hydrogen-bonded dimers in chloroform and supramolecular polymerization did not occur through the triple hydrogen-bonding interactions (Scheme 2).

Wide Angle X-ray Scattering (WAXS) experiments

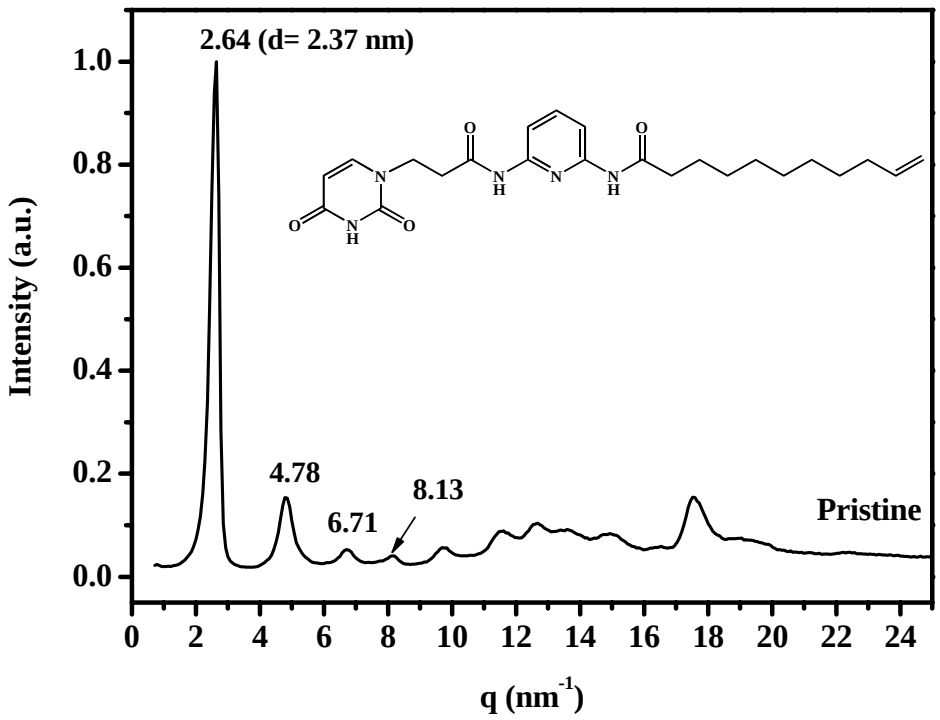


Figure S10: WAXS spectrum of pristine U-DPy.

The pristine U-DPy exhibited sharp crystals halos centered at q = 2.64 nm^{-1} as shown in the WAXS patterns in Figure S10. The scattering peaks suggested a crystal structure for pristine U-DPy, which constituted a disordered array.

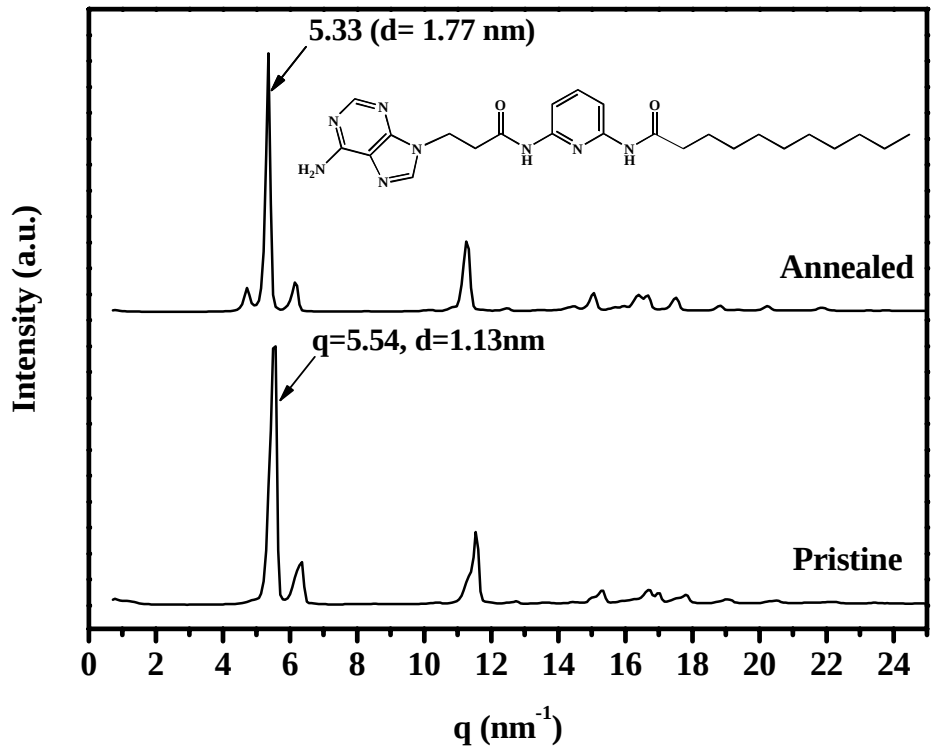


Figure S11: WAXS spectra of pristine and annealed A-DPy (annealing conditions: 160°C, for 1 h under vacuum).

As a control experiment, pristine and annealed A-DPy (Figure S11) displayed peaks at q = 5.54 and 5.33 nm^{-1}, respectively (d = 1.13 and 1.77 nm, respectively), indicative of unspecified structures at a relatively large size scale. The observed spacing indicated that the intermolecular A···DAP interactions did not occur and the self-assembly behavior was not observed.

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