## **Supporting Information for**

## Hybrid Nanocrystals of Small Molecules and Chemically Disordered Polymers

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## **Materials and Methods**

<u>Chemicals</u>: Perylene-3,4,9,10-tetracarboxylic dianhydride, 1,5-diazabiciclo(5.4.0)undec-7-ene, *p*-toluenesulfonic acid monohydrate, 3-picoline, *n*-butanol and 1-bromobutane were purchased from Acros Organics and used as received. *N*-Boc-1,5-diaminopentane was purchased from Chem-Impex International and used as received. Poly(ethylene-*alt*-maleic anhydride) with an average molecular weight  $M_w$  100,000–500,000 was purchased from Sigma-Aldrich and used as received. Polyoxyethylene bis(amine) (M.W. 3,400) was purchased from Alfa Aesar. All other common solvents and reagents were purchased from Fisher Scientific and used as received unless noted otherwise. Water used for co-assembly experiments was passed through a Barnstead Nanopure (D3750 hollow fiber filter, 0.2 µm pore size) and UV-irradiated to achieve 18.2 MΩ-cm purity before use. Compounds CA **1**, CA **3**<sup>1</sup> and the Na<sub>2</sub>[Mo<sub>3</sub>S<sub>13</sub>]•5H<sub>2</sub>O catalyst<sup>2,3</sup> were prepared according to literature procedures.

Instrumentation: <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker Advance III HD system (500 MHz) equipped with a TXO Prodigy probe. ESI-MS were performed on a Bruker Amazon-SL. UV–Vis absorption spectroscopy was performed in a 0.05 mm path length, closed demountable quartz spectrophotometer cell (Starna Cells) using an Ocean Optics OEPro Spectrophotometer equipped with a DH-2000-Bal lamp and qpod 2e temperature control sample chamber. Fluorescence spectroscopy photoluminescence spectra were all acquired with a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) with a 2 nm slit width. All spectra were acquired at room temperature using a 1 cm quartz cuvette. Transmission electron microscopy (TEM) imaging was performed on a JEOL 1230 microscope operating at 100 kV and equipped with a Gatan 831 CCD camera. SAXS and WAXS experiments were performed at Beamline 5-ID-D in the DuPont-Northwestern-Dow Collaborative Access team (DND-CAT) Synchrotron Research Center at the Advanced Photon Source, Argonne National Laboratory using the triple detector setup<sup>4</sup>. X-ray energy of 17 keV for room temperature measurements and 10 keV for variable temperature (VT) measurements were selected using a double-crystal monochromator. Unless otherwise noted, measurements of solution samples were either placed in a vacuum flow cell comprising of a 1.5 mm quartz capillary connected to a syringe pump that induced sample oscillation during the X-ray exposure, or placed in 1.5 mm quartz capillaries (Charles Supper Co.) which were then inserted into the beam path in air for measurements. The acquired 2D scattering images were azimuthally integrated using the GSAS-II software<sup>5</sup> to yield the corresponding 1D scattering intensity versus the scattering vector magnitude, q, defined as  $q=4\pi\sin\theta/\lambda$  where  $\theta$  is half of the total scattering angle, and  $\lambda$  is the X-ray wavelength. In the case of vacuum flow cell experiments, buffer signals and empty capillary signals were obtained prior to sample measurements, and they were used to quantitatively subtract the buffer and capillary scattering. In the case of static sample measurements, scattering intensity of the buffer solvent was separately collected using a similarly sized capillary, and was used with a scaling factor to subtract signals from the capillary and the buffer. In order to observe the Bragg reflections, the resulting scattering curves in the wide-angle region (q > 0.8 Å<sup>-1</sup>) were spline baseline-subtracted for broad peaks in measurements taken in static capillaries. Gel Permeation Chromatography (GPC) was performed on a dedicated system with Water PBS as default solvent and Yara  $3 \mu m$ , SEC-2000,  $300 \times 7.8 mm$  column (Phenomenex p/n OOH-4512-KO using the Agilent VWD UV Detector, MALS (18 Angles Dawn Heleos II), and the Differential Refractive Index (OptiLab T-rex). Atomic force microscopy (AFM) was performed on a Veeco Dimension icon scanning probe microscope (Veeco), Nanoscope V Controller (Bruker), with the SNL-10 A probes (nominal tip radius 2 nm, force constant 0.35 N/m,

Bruker). *Rheological measurements* were performed on an Anton Paar MCR302 rheometer with a P-PTD200 Peltier system for temperature control.

Synthesis of Perylene-3,4,9,10-tetracarboxylic tetrabutylester (1): Compound was synthesized according to a literature procedure<sup>6</sup>. Perylene-3,4,9,10-tetracarboxylic dianhydride (20.0 g, 51.0 mmol), 1,5-diazabiciclo(5.4.0)undec-7-ene (30.5 mL, 204 mmol) and *n*-butanol (37.3 mL, 408 mmol) were dissolved in *N*,*N*<sup>2</sup>-dimethylformamide (DMF) (0.25 L, dried on a solvent still over calcium hydride) and stirred at 60°C for 30 min. Then, a solution of 1-bromobutane (43.8 mL, 408 mmol) in DMF (0.25 L) was added and the mixture was stirred overnight at 60°C. The mixture was allowed to cool down to room temperature, poured into H<sub>2</sub>O (2.0 L) and left stirring for 15 min. The precipitate was filtered, washed with H<sub>2</sub>O (2 × 0.5 L) and dried under vacuum. Purification by column chromatography (SiO<sub>2</sub>, 40-63 µm, CH<sub>2</sub>Cl<sub>2</sub>) afforded product **1** as bright orange solid (30.3 g, 91% yield). <sup>1</sup>**H-NMR** (500 MHz, Chloroform-*d*): 8.28 (d, *J* = 8.0 Hz, 4H), 8.03 (d, *J* = 7.8 Hz, 4H), 4.34 (t, *J* = 6.8 Hz, 8H), 1.90–1.68 (m, 8H), 1.52–1.38 (m, 8H), 0.99 (t, *J* = 7.4 Hz, 12H). <sup>13</sup>C-NMR (126 MHz, Chloroform-*d*):  $\delta$  168.67, 132.99, 130.49, 130.46, 128.99, 128.81, 121.44, 65.47, 30.81, 19.43, 13.97. Characterization in accordance with literature <sup>6,7</sup>.

Synthesis of Perylene-3,4,9,10-tetracarboxylic monoanhydride dibutylester (2): Compound was synthesized according to a modified literature procedure<sup>8</sup>. Perylene-3,4,9,10-tetracarboxylic tetrabutylester **3** (10.0 g, 15.3 mmol) and *p*-toluenesulfonic acid monohydrate (2.9 g, 15.3 mmol) were suspended in a mixture of toluene/hexane (90 mL, 5:1  $\nu/\nu$ ) and heated to 100°C for 5 h. The mixture was left to cool down to room temperature, then the solid was filtered, washed with boiling hexane (3 × 100 mL) and acetonitrile (3 × 100 mL). Finally, the solid was dried under vacuum to obtain product **2** as bright red solid (6.88 g, 86% yield). <sup>1</sup>H-NMR (500 MHz, Chloroform-*d*):  $\delta$  8.65 (d, *J* = 7.9 Hz, 2H), 8.53 (d, *J* = 8.3 Hz, 2H), 8.51 (d, *J* = 7.8 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 4H), 1.83-1.77 (m, 4H), 1.52-1.48 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*):  $\delta$  168.29, 160.52, 137.53, 133.83, 133.01, 131.79, 130.63, 129.50, 126.64, 123.71, 122.37, 118.24, 65.94, 30.82, 19.47, 14.00. Characterization in accordance with literature <sup>8</sup>.

Synthesis of Perylene-3,4-dicarboxylic dibutylester (3): Compound was synthesized according to a modified literature procedure<sup>9</sup>. A mixture of copper powder (9.5 g, 149.5 mmol) in 3-picoline (77.0 mL) was heated at 80°C for 24 h under N<sub>2</sub>. Then, perylene-3,4,9,10-tetracarboxylic monoanhydride dibutylester 2 (5.23 g, 10.0 mmol) was added and the mixture was heated at 175°C for 12 h, under N<sub>2</sub>. The 3-picoline was distilled off and the residual solid was taken up with CH<sub>2</sub>Cl<sub>2</sub> and passed through a SiO<sub>2</sub> plug (CH<sub>2</sub>Cl<sub>2</sub>). Purification by column chromatography (SiO<sub>2</sub>, 40-63 µm, hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:1  $\nu/\nu \rightarrow$  CH<sub>2</sub>Cl<sub>2</sub>) afforded product **3** as bright yellow solid (2.8 g, 91% yield). <sup>1</sup>H-NMR (500 MHz, Chloroform-*d*):  $\delta$  8.31 (d, *J* = 7.5 Hz, 2H), 8.27 (d, *J* = 7.9 Hz, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 6.9 Hz, 4H), 1.83–1.69 (m, 4H), 1.52–1.40 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H).

Synthesis of Perylene-3,4,dicarboxylic monoanhydride (4): Compound was synthesized according to a modified literature procedure<sup>9</sup>. A suspension of perylene-3,4-dicarboxylic dibutylester **3** (1.0 g, 2.2 mmol) and *p*-toluenesulfonic acid monohydrate (1.1 g, 6.6 mmol) in toluene was heated to 100°C for 3 h. During the reaction a dark purple solid formed. The mixture was left to cool down to room temperature, then the solid was filtered and washed with CH<sub>3</sub>OH ( $3 \times 50$  mL). The solid was dried under high vacuum to produce a dark, purple solid product (0.7 g, 94% yield) that was carried over directly to the next reaction.

Synthesis of *N*-(5-Boc-aminopentyl)perylene-3,4-dicarboximide (5): *N*-Boc-1,5-diaminopentane (1.7 g, 8.4 mmol) and perylene-3,4,dicarboxylic monoanhydride **4** (1.0 g, 4.7 mmol) were suspended in dry DMF (50 mL, dried on a solvent still over calcium hydride) and dry DIPEA (0.8 ml, 8.3 mmol) in a 100 ml round bottom flask. The reaction mixture was stirred at 80°C for 4 h under N<sub>2</sub> to produce a dark, red solution. Once cooled to room temperature, the reaction mixture was diluted with DCM (300 ml) then washed with 2.5% potassium bisulfate (2 × 500 ml), water (2 × 500 ml) and brine (1 × 500 ml). The DCM layer was dried using magnesium sulfate, filtered and solvent removed via rotary evaporation. The compound was purified was by silica gel flash column chromatography by dry loading the sample and applying a slow, solvent gradient from 1:100 MeOH/DCM to 5:100 MeOH/DCM to yield product **5** as a bright, red powder (2.1 g, 84% yield). <sup>1</sup>**H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.71 (dd, *J* = 7.8, 4.7 Hz, 4H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 2H), 4.06 (t, *J* = 7.4 Hz, 2H), 2.92 (q, *J* = 6.6 Hz, 2H), 1.64 (q, *J* = 7.6 Hz, 2H), 1.43 (q, *J* = 7.2 Hz, 2H), 1.34 (m, 11H). **MS-ESI:** Expected *m*/z: 507.23 [M+H]<sup>+</sup>, found 506.22 [M+H]<sup>+</sup>.

<u>Synthesis of *N*-(5-aminopentyl)perylene-3,4-dicarboximide (6): *N*-(Boc-aminopentane) perylene-3,4-dicarboximide (5) (1 g, 2 mmol) was added to a solution of DCM (40 ml) and TFA (40 ml) and stirred at room temperature for 2 h to produce a dark, purple solution. The solvent was removed via rotary evaporation to produce the trifluoroacetic acid salt of the final product as a dark, purple powder (1.02 g, 99% yield). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.43 (d, *J* = 7.6 Hz, 2H), 8.38 (d, *J* = 8.1 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 3H), 7.59 (t, *J* = 7.8 Hz, 2H), 4.00 (t, *J* = 7.4 Hz, 2H), 2.82 (m, 2H), 1.64 (m, 4H), 1.48 – 1.34 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  163.31, 136.76, 134.09, 131.38, 131.20, 129.18, 128.62, 127.58, 127.23, 126.15, 124.75, 121.06, 120.44, 39.22, 27.53, 27.30, 23.89. MS-ESI: Expected *m*/z: 407.18 [M+H]<sup>+</sup>, found 407.19 [M+H]<sup>+</sup>.</u>

<u>General Procedure for Functionalization of Poly(ethylene-alt-maleic anhydride) (PEAMA):</u> In a typical experiment, stock solutions of <u>N-(5-aminopentyl)perylene-3,4-dicarboximide</u> (6) in dry DMF at 50 mM concentration and PEAMA in dry DMF (dried on a solvent still over calcium hydride) at a concentration of 40 mg/ml were prepared separately to ensure full dissolution of the starting compounds. Polymer functionalization occurred by adding the desired amount of <u>N-(5-aminopentyl)perylene-3,4-dicarboximide</u> (6) solution to a vigorously stirred PEAMA solution, then adding 2 eq. of dry DIPEA to initiate the reaction. The reaction vessel was stirred for 18 h at room temperature then the polymer was precipitated in 1 M HCl to yield a dark, red powder. The polymer was then immediately resuspended in a NaOH solution (pH 7–9) and heated to 80°C for 18 h to hydrolyze any remaining anhydride moieties. The aqueous polymer solution was then dialyzed for 72 h against MilliQ water using dialysis tubing with a molecular weight cut-off of 12–14 kDa. The final products were isolated by lyophilization to yield a bright red powder. The

polymer functionalization (f) was characterized with <sup>1</sup>H NMR in DMSO- $d_6$  by the ratio ( $\beta$ ) between the peak integration from the aromatic protons (C) and the alkyl polymer backbone protons (A) (Figure S4) such that  $f = 4\beta/(10 - 6\beta)$ . The polymer functionalization was also characterized by the absorbance spectra of the polymer in DMSO using the molar absorptivity of the PMI chromophore (CA 1) in DMSO. Aqueous GPC of the 0% functionalized "parent" polymer (i.e., poly(ethylene-alt-maleic acid)) measured  $M_n = 248.9$  kDa and D = 1.13 with respect to a standard polymer calibration curve. The functionalized polymer was further characterized by UV-Vis absorption and fluorescence spectroscopy in DMSO and 50 mM NaCl<sub>(aq)</sub> (Figure S6). Fluorescent measurements were taken at a concentration where the absorbance at the excitation wavelength was matched between samples. In DMSO, the polymer is highly fluorescent, which is indicative that the chromophores are in a "monomeric" non-assembled state when covalently immobilized on the polymer. As the degree of PMI functionalization increased, the fluorescence intensity decreased, which can be attributed to a higher probability of the chromophores interacting along the polymer backbone and leading to a quenching in their emission. In 50 mM NaCl<sub>(aq)</sub>, the polymers all show a dramatic decrease in fluorescence intensity, which is indicative that the polymer chain has collapsed into a self-assembled structure where the chromophores are aggregated thereby leading to fluorescence quenching.

<u>Co-Crystallization of Polymer 2 and CA 1:</u> Samples were prepared by mixing aqueous solutions of polymer 2 (5 mM PMI chromophore, 50 mM NaCl, pH adjusted to pH 6.8–7.3) and CA 1 (5 mM PMI chromophore, 50 mM NaCl, 5 mM NaOH) at different co-assembly ratios  $\phi$ , then sonicating and vortex mixing to ensure homogenous mixing. Once mixed, the samples were annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples in a water bath to room temperature over 18 h. See Table S2 for full details on sample preparation and pH conditions.

Electron Microscopy of the Changes in the Nanostructure Morphology: Samples were prepared by mixing aqueous solutions of polymer 2 at 10%, 20%, or 30% functionalization (5 mM PMI chromophore, 50 mM NaCl, pH adjusted to 6.8-7.3) and CA 1 (5 mM PMI chromophore, 50 mM NaCl, 5 mM NaOH) at different co-assembly ratios ( $\phi$ ) then sonicating and vortex mixing to ensure homogenous mixing. Once mixed, the samples were then annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. For conventional TEM, these samples were diluted by a factor of 5 in 50 mM NaCl then 5 all were deposited on a pure carbon film deposited on a copper grid (CF-300-Cu, Electron Microscopy Sciences). Excess liquid was wicked away and the sample was left to dry for 1 min, then 5 µL of a 1 wt% uranyl acetate (UA) solution was added to stain the samples. Again, excess liquid was wicked away and the sample was left to dry for 1 min before washing with mQ water. Cryo-TEM samples were prepared using Vitrobot Mark IV (FEI) under room temperature with 95% humidity. After diluted five fold with MilliQ water from 10 mM stock, 5 µL of the resulting solution was applied onto the shiny side of 300 mesh lacey carbon grid (Electron Microscopy Sciences), blotted twice, plungefroze with liquid ethane and transferred immediately into liquid nitrogen reservoir for storage. Images were taken by a Gatan 831 CCD camera bottom mounted on JEOL1230 microscope at 100 kV accelerating voltage. The nanostructure widths and aspect ratios were measured in ImageJ<sup>10</sup>.

<u>Co-Crystallization of Polymer 2 and CA 3</u>: Samples were prepared by mixing aqueous solutions of polymer 2 (5 mM PMI chromophore, 50 mM NaCl, pH adjusted to 6.8–7.3) and CA 3 (5 mM

chromophore, 50 mM NaCl, 5 mM NaOH) at different co-assembly ratios ( $\phi$ ) then sonicating and vortex mixing to ensure homogenous mixing. Once mixed, the samples were then annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. Control experiments with 0%-functionalized polymer (i.e., poly(ethylene-*alt*-maleic acid)) were performed with See Table S2 for full details on sample preparation and pH conditions.

As  $\phi$  increases from 0 to 1 we see distinct transitions in the crystal structure of the hybrid covalentsupramolecular polymer that forms after annealing between polymer 2 and CA 3. From  $\phi = 0$  to  $\phi = 0.5$ , the scattering peaks from the WAXS of the  $\alpha$ -crystal phase show an increase in the intensity and decrease in the full width at half maximum (FWHM) indicating that free CA 3 incorporates with polymer 2 to form the  $\alpha$ -phase. As the co-assembly ratio increases from  $\phi = 0.5$ to 0.7–0.9 we see a second distinct region in the phase-space where the  $\gamma$ -phase associated with CA 3 begins to nucleate and emerge in the scattering pattern as the  $\alpha$ -phase begins to decrease in intensity.<sup>1</sup> The emergence of the  $\gamma$ -phase is most clear from a new scattering peak at q = 0.65 Å<sup>-1</sup> in the mid-angle X-ray scattering (MAXS) and a new absorbance peak at 740 nm that is associated with the crystallinity of the  $\gamma$ -phase. Finally, from  $\phi$  in the range 0.7–0.9 to  $\phi = 1.0$  the  $\gamma$ -phase is the only crystal phase detected in the WAXS pattern and absorption spectra indicating that the PMI chromophores on the covalent polymer 2 are incorporated with the  $\gamma$ -phase formed by CA 3. Another interesting feature of the co-crystallization of polymer 2 and CA 3 can be seen when comparing the MAXS patterns and absorption spectra between the  $\gamma$ -phase hybrid bonding polymers ( $\phi = 0.9$ ) and the  $\gamma$ -phase supramolecular polymer ( $\phi = 1.0$ ). The MAXS peak shifts from q = 0.60 Å<sup>-1</sup> to q = 0.65 Å<sup>-1</sup> and the crystalline absorbance peak shifts from 740 to 760 nm as the co-assembly ratio increases, indicating that the  $\gamma$ -phase hybrid bonding polymer has slightly different intermolecular distances than the  $\gamma$ -phase supramolecular polymer. This change in crystal structure formed by the hybrid bonding polymer serves as further evidence that polymer 2 and CA **3** are co-crystallizing.

<u>Coarse-Grained Model Details:</u> Using molecular dynamics (MD) simulations we investigated selfassembly of perylene monoimide (PMI) chromophore amphiphile (CA) molecules shown in Figure S29. In the following we refer to these molecules as chromophores. Molecules are attached to a short linker which is either terminated by a negatively charged carboxyl group or is attached to a polymer backbone.

To capture the essential properties of the chromophore molecule we constructed a coarse-grained model. The model aims to accurately represent excluded volume,  $\pi$ - $\pi$  stacking interaction and electrostatic contributions to the chromophore-chromophore interaction. The excluded volume was modeled using 13 spheres connected into a rigid body as shown in Figure S29. The sphere-sphere interaction of green and red beads was captured by a standard shifted-truncated Lennard-Jones (LJ) interaction with size  $\sigma = 3.2$  Å, cutoff  $r_c = 3.5\sigma$  and well depth  $\varepsilon_{hf} = 0.6k_BT$ . These parameters characterize the van der Waals radius of the chromophore molecule and the small hydrophobic attraction. As we show below, inclusion of the (weak) hydrophobic attraction is crucial for the self-assembly as the electrostatic interactions alone are not sufficiently strong to induce sheet formation in the model.

The dipole-free chromophore dimerization interaction was approximated by the isodesmic binding of symmetric perylene diimides in water, which is experimentally known to be  $\Delta G \sim 45$  kJ/mol<sup>11</sup>,

corresponding to  $18k_{\rm B}T$  at room temperature. Both the hydrophobic interaction and the  $\pi$ - $\pi$  stacking contribute to this interaction. We chose to attribute  $\varepsilon_{\rm hf} = 0.6k_{\rm B}T$  to hydrophobic interaction per bead, which for 12 face beads adds to about  $7k_{\rm B}T$  of direct interaction with neighbors also contributing a few  $k_{\rm B}T$ . The remaining  $10k_{\rm B}T$  was attributed to stacking ( $\pi$ - $\pi$ ) interaction described by the central (pink) bead having a much stronger attractive Lennard–Jones interaction  $\varepsilon_{\pi} = 10k_{\rm B}T$  with other central beads. The decomposition of the total dimerization interaction into directional and omnidirectional interaction is an approximation that achieves strong face–face interaction and weaker edge–edge interaction between PMI molecules. The relative strength of these interactions is the only free parameter in our model. Changing the relative values affects the aspect ratio of the final assembled structure. The values ( $\varepsilon_{\rm hf} = 0.6k_{\rm B}T$  and  $\varepsilon_{\pi} = 10k_{\rm B}T$ ) were chosen such that the aspect ratio of the pure supramolecular PMI structure (no covalent polymer,  $\phi = 1$ ) matches the experimental value of about  $\alpha \sim 5$  (see Table S3).

The four corner spheres were charged with  $q = \pm 0.1q_0$ , where  $q_0$  is the unit electron charge, and were positioned on a rectangle with sides a = 7.1 Å and b = 5.2 Å. These charge values and geometry accurately capture the electrostatic dipole and octupole moments of the molecule as computed by DFT calculations (details provided below). The electrostatic interaction between chromophores is not screened (relative permittivity  $\varepsilon_r = 1$ ) in order to accurately capture the electrostatic energy of the assembled sheet-like crystal structure.

We also included an additional bead (top purple sphere in Figure S29) accounting for the alkyl tail. This bead is bonded to the chromophore molecule via a flexible harmonic bond  $U_b(r) = K_b(r - r_0)^2$  (with spring constant  $K_b = 32k_BT/\sigma^2$  and rest length  $r_0 = 1.875\sigma = 6$  Å) and a cosine angle potential  $U_{\theta}(\theta) = K_{\theta}[1 - \cos(\theta - \theta_0)]$  (with  $K_{\theta} = 2k_BT$  and  $\theta_0 = \pi$ ). The bead is negatively charged due to the dissociated carboxylic end group with  $q = -q_0$  and interacts with other tail beads via a Yukawa screened electrostatic potential with Debye length  $l_D = 4\sigma$ , reflecting that this tail bead is assumed to be surrounded by water with monovalent salt concentration of  $c_{NaCl} = 50$  mM. The tail (purple) beads interact with all other types of beads by a purely repulsive shifted-truncated Lennard-Jones potential with  $\varepsilon_{rep} = k_BT$  and  $r_c = 2^{1/6}\sigma$ . To show clearly how different types of spheres interact with each other, we summarize the pairwise interactions in Table S3. This CG model was validated to reproduce accurate structures, lattice parameters, and aspect ratios of the pure PMI nanostructures.

The polymer backbone is modeled as a permanently (covalently) bonded bead–spring chain. Each bead is represented as a charged (shifted-truncated Lennard–Jones) sphere with size  $\sigma_p = \sigma$  and charge  $q = -q_0$ , such that each monomer is represented by a bead. The persistence length of the free polymer alone is  $l_p \sim 70$  Å at 50 mM NaCl salt concentration <sup>12</sup>. The model uses a distance harmonic potential between adjacent beads  $U_b = K_b(r_{ij} - r_0)^2$  (with  $K_b = 32k_BT/\sigma^2$  and  $r_0 = 1.25\sigma \sim 4$  Å) and a cosine angular potential  $U_{\alpha} = K_{\alpha}[1 - \cos(\alpha - \alpha_0)]$  (with  $K_{\alpha} = 16k_BT$  and  $\alpha_0 = \pi$ ), yielding the correct persistence length  $l_p = K_{\alpha} r_0/k_BT$ .

<u>Electrostatic Multipole Mapping</u>: The PMI chromophore is a planar molecule with a dipole moment 7.1 D, where D = 0.208  $q_0$ Å. The dipole moment ( $Q_x = 7.1$  D) of CA 1 was computed using DFT by replacing the L<sub>5</sub>-COOH with a methyl group. The structure was optimized using the Gaussian 16 program package <sup>13</sup>, followed by frequency calculations on the optimized structures, which confirmed that the optimized structure is stable. DFT calculations were performed using the

hybrid functional B3LYP <sup>14–16</sup> and the 6-31G(d,p) basis set. Quadrupole moments of the chromophore molecule are rather small with  $Q_{xx} = -3.7$  DÅ,  $Q_{yy} = -2.9$  DÅ,  $Q_{zz} = -6.5$  DÅ. However, the relevant (i.e., non-vanishing) octupole moments are much larger with  $Q_{xxx} = 124$  DÅ<sup>2</sup>,  $Q_{xyy} = 84$  DÅ<sup>2</sup>,  $Q_{xzz} = -33$  DÅ<sup>2</sup>. In the following, we will neglect quadrupole moments and only take into account dipolar and octupolar contributions. The simplest point charge distribution that satisfies the dipole and octupole moments consists of four charges arranged on a rectangle with sides a = 7.1 Å and b = 5.2 Å. Each point charge has a magnitude of  $q = Q_x/(2a) = 0.1q_0$ . This charge distribution is captured by the four-point charges shown as red spheres in Figure S29.

Simulation Methods: The simulations were performed using the open-source MD package LAMMPS in the NVT ensemble. Typical runs contained 500 chromophore molecules in a 3D periodic cubic box with box length  $200\sigma$ . The initial configuration was obtained by randomly positioning chromophore molecules in the box. We applied a Langevin thermostat with damping parameter 100 $\tau$  and time unit  $\tau = \sigma (m/k_{\rm B}T)^{1/2}$  defined by the (arbitrary) mass of the individual beads *m*. All simulations were conducted with a time step  $\Delta t = 0.005\tau$ . To prevent the system from getting kinetically trapped, we annealed it for  $t_{tot} = 4 \cdot 10^8$  time steps, where a linear temperature ramp was applied starting with the highest temperature at  $T^{\text{high}} = 3T$  and ending with  $T^{\text{low}} = T$ . The temperature at time t is thus  $T_t(t) = T^{\text{low}} + (T^{\text{high}} - T^{\text{low}})(1 - t / t_{\text{tot}})$ . Statistical averages of the measured quantities (e.g., radial distribution function or the radius of gyration tensor) were obtained in the final 10<sup>6</sup> steps of the simulation. The relatively short sampling time was used because we found that the configurations of the nanostructures are arrested at low temperature  $(T_t < 1.5T^{\text{low}})$  and do not evolve. Note that all interaction potentials, except for the backbone bending potential, remained constant during the annealing process. The backbone bending prefactor is time dependent and determined by the time-dependent temperature  $T_t$ ,  $K_{\alpha}(t) =$  $16k_BT_t(t)$ , which ensures that the persistence length of the polymer remains constant during the annealing process.

For the annealing simulation results presented in Figure 4 of the main text, we started with the mixture of the equilibrium structures obtained at  $\phi = 0$  and  $\phi = 1$ . We first heated the system for  $3 \cdot 10^8$  steps where the reduced temperature  $T^* = T_t/T$  increased linearly from 1 to 2.2. This was followed by the cooling process for another  $3 \cdot 10^8$  steps where the temperature linearly dropped from  $T^* = 2.2$  to  $T^* = 1$ . The formation and aspect ratio of the structures was reproducible (Figure 3j) and increasing the annealing time did not noticeably affect the resulting structures, which led us to conclude that the obtained structures are sufficiently equilibrated. To count the number of bonding interactions between different species, we adopted a cut-off distance of 1.5\sigma between the central (pink) beads of the chromophores. Fluctuations in the number of bonding average over each window of less than 50 data points.

The simulation time scale can be estimated from the diffusion constant of individual chromophores. Assuming that the Stokes–Einstein relation holds and that the chromophores are about 1 nm in radius (including the solvation shell), we obtain a diffusion constant  $D = 2 \cdot 10^9 \sigma^2/s$ . Calculating the mean square displacement of individual free chromophore molecules from simulations, we obtain the diffusion constant  $D_{sim} = 20 \sigma^2/\tau$ . Equating  $D_{sim} = D$  we obtain the simulation time unit,  $\tau \approx 10$  ns.

Estimation of the Aspect Ratio: The aspect ratio of the simulated structures was determined from the calculated radial distribution function of the central (pink) beads, see Figure S29. Specifically, the number of "face"  $n_f$  and "side"  $n_s$  neighbors was determined by integrating the radial distribution function

$$n_{\rm f} = \int_{0.8\sigma}^{1.3\sigma} 4\pi r^2 g(r) dr$$

and

$$n_{\rm s} = \int_{2.25\sigma}^{2.85\sigma} 4 \,\pi \, r^2 g(r) dr$$

where the integral bounds correspond to the minima in the radial distribution function. Note that  $n_s$  captures both the nearest as well as second-nearest side neighbors. The ratio of the neighbors is  $I = \frac{n_s}{n_f}$ . This ratio maps to a specific aspect ratio if we assume that the structure is of rectangular shape. The number of chromophores per nanostructure length (in the face direction) n can be obtained by solving the quadratic equation:

$$\frac{3n^2}{l} + \left(N_{\rm c} - \frac{3N_{\rm c}}{l} - \frac{2}{l}\right)n + \left(\frac{2N_{\rm c}}{l} - N_{\rm c}\right) = 0$$

where  $N_c$  is the total number of chromophores in the structure. The aspect ratio  $\alpha$  and the width of the structure *w* are

 $\alpha = \frac{a}{bN_c}n^2$ 

and

$$w = \frac{N_{\rm c}b}{n}$$

where  $a = 1.05\sigma$  and  $b = 2.4\sigma$  determine the rectangular dimensions of a single chromophore, which were estimated from the radial distribution function peak positions. The calculated aspect ratio provides a convenient way to quantify the morphology of the nanostructures shown in Figure S30.

Simulations of Shear and Yielding: The radius of gyration tensor was calculated from the final structures obtained from annealing simulations. The structures were then oriented according to their eigenvectors. The eigenvector with the largest eigenvalue (along the structure length) was oriented with the *x*-axis and the eigenvector with the second largest eigenvalue (along the ribbon width) was oriented along the y-axis. The center of mass of the structure was placed at x = 0. All chromophore molecules with coordinates  $x < x_{\min}$  were frozen, representing the condition of being "clamped" (grey colored chromophores in Fig. 5 in the main text). Conversely, all chromophores with at  $x > x_{\max}$  are designated as a single rigid body (also colored in grey in Fig. 5 in the main text), to simulate the chromophores being clamped together, but allowed to move as a single rigid body. A force  $f_y$  was applied to the center of mass of this rigid body in the direction of the *y*-axis. Non-clamped parts of the structure (chromophores with initial position  $x_{\min} \le x \le x_{\max}$  as well as all polymer backbones) were simulated using the MD scheme described above.

This setup effectively simulates the response of the structures to shear in the *xy* plane. Shearing simulations were performed using a slow force ramp  $\frac{df_{xy}}{dt} = 2 \cdot 10^{-2} \frac{k_B T}{\sigma \tau}$ . Thus, we obtained the shear curves by monitoring the center of mass coordinate *y* of the clamped rigid body to which the force is applied. The yield point was defined as the force at which the structure breaks into two disjoint structures A and B, where every chromophore in structure A is at least a distance  $2\sigma$  from every chromophore in structure B. The shear force curves are shown in Figure S51. The data in Fig. 5 in the main text represent averages of 5 different positions of the clamp  $\frac{x_{\min}}{\sigma} = \{-18, -16, -14, -12, -10\}$ , with  $x_{\max} = x_{\min} + 32\sigma$ .

Using the simulation timescale  $\tau \approx 10$  ns we estimate the total time to break a structure at  $\tau_{shear} \sim 0.1$  ms. Although this time scale is about three orders of magnitude faster than the experimental conditions for measuring the bulk shear modulus ( $\omega = 10s^{-1}$ ), the simulated shear rate is significantly slower than the timescale of single molecule reorganization. This leads us to conclude that the simulated shear results are able to partly elucidate the mechanism that leads to non-monotonic shear modulus dependence on the co-assembly ratio.

<u>Variable-Temperature Wide-Angle X-Ray Scattering Experiments</u>: Samples were prepared by making two solutions containing polymer **2** at 30% functionalization (9.6 mM PMI chromophore, 50 mM NaCl, pH = 7.22) and CA **1** (9.6 mM PMI chromophore, 50 mM NaCl, 5 mM NaOH). These two solutions were annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. The annealed solutions were then mixed at different values of  $\phi$ , sealed within a vacuum capillary, and heated at 1°C per minute from 32°C to 86°C taking *in-situ* WAXS patterns every 10 min. The samples were held at 86°C for 30 min than cooled to 32°C at 1°C per minute again taking *in-situ* WAXS patterns every 10 min.

<u>Time-Dependent UV–Vis Experiments</u>: Samples were prepared by making two solutions containing polymer **2** at 30% functionalization (10 mM PMI chromophore, 50 mM NaCl, pH adjusted to 7.22) and CA **1** (10 mM PMI chromophore, 50 mM NaCl, 5 mM NaOH). These two solutions were annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. The separately annealed solutions were then mixed to create solutions at  $\phi = 0.3$  and  $\phi = 1.0$ . Absorption spectra were measured with a 0.1 mm path length flow cell cuvette that was pre-heated to 95°C. Upon injecting samples into the flow cell cuvette, absorption spectra were taken every second to characterize the formation of the hybrid bonding polymer at 95°C. In Figure S39, we monitored the melting of the  $\beta$ -phase formed by CA **1** at  $\phi = 1.0$  by monitoring the decay of the peak maximum at 440 nm over time. Results indicate that  $\beta$ -phase formed by CA **1** fully melts over the 1 hour annealing time reaching a plateau around 40 minutes. In Figure S40, we monitor both the growth of  $\alpha$ -phase formed by the HBP at  $\phi = 0.3$  and the melting of the  $\beta$ -phase formed by CA **1** at  $\phi = 1.0$ . The growth of the  $\alpha$ -phase was monitored by the absorbance peak at 430 nm and the melting of the  $\beta$ -phase was monitored by the absorbance peak at 570 nm, since the 440 nm peak can be convoluted with the growth of the  $\alpha$ -phase.

<u>Nanomechanical Measurements</u>: AFM indentation and fracture tests were performed on a Veeco Dimension Icon scanning probe microscope (Veeco), Nanoscope V Controller (Bruker), at room temperature. The SNL-10 A probes (nominal tip radius 2 nm, Bruker) were used with ScanAsyst in air imaging mode (Peakforce Force Tapping) at 2 kHz with an amplitude of 150 nm. The

deflection sensitivity (44.97~46.63 nm/V) was measured against a sapphire substrate in air. The spring constant of the cantilever (0.2190~0.2785 N/nm) was obtained by thermal tune method in air. The samples were prepared by dropping the HBP solution on fresh mica substrates and washed twice with Milli-Q water before dried in air. To obtain the force-separation curves, nano-indentation was performed in "point and shoot" mode with ramp size/height of 50 nm and ramp velocity of 100 nm/s. The fracture force is determined at the inflection point on the approach part of a force curve. The inflection points at negative forces were not considered. When multiple inflection points were visible only the first major inflection point was considered to measure the mechanical strength of the material. Self-healing tests were performed in "point and shoot" mode with the same experimental parameters as applied in fracture tests. The force curves of multi-cycle tests were obtained by separate indentation steps after different waiting time of 30 s, 60 s and 300 s without changing the location of the AFM tip (Fig. S46). Indentation rate: 200 nm/s, humidity: 41~45%. The raw force curves and AFM images of the nanostructures used for the healing tests are shown for  $\phi = 1.0$  (Fig. S47),  $\phi = 0.8$  (Fig. S48) and  $\phi = 0.5$  (Fig. S49).

<u>Gelation Experiments</u>: Stock solutions of 10% functionalized polymer **2** and PMI CA **1** from  $\phi = 0$  to  $\phi = 1$  (12.8 mM of PMI chromophore, 50 mM aq. NaCl) were adjusted to pH 6.3 then were annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. The nanostructures were then gelled by crosslinking them with polyoxyethylene bis(amine) (M.W. 3,400) through an EDC/NHS coupling reaction. A typical procedure is as follows. 600 µL of the annealed 10% PMI-Functionalized Polymer and PMI CA solution were mixed with 38.4 µL of a 2 M aqueous solution of 1-ethyl-3-(3 dimethylaminopropyl) carbodiimide (EDC) and 38.4 µL of a 2 M aqueous solution of *N*-hydroxysuccinimide (NHS). The solution was vortexed and then allowed to activate at room temperature for 10 min. Next, 38.4 µL of a 100 mM aqueous solution of polyoxyethylene bis(amine) was added. The solution was vortexed and allowed to react overnight (~18 h).

Rheological measurements were performed using a cone and plate fixture with a 25 mm radius and 106  $\mu$ m gap height. In a typical experiment, 150  $\mu$ L of the gelled nanostructures was placed on the sample stage. The plunger was then lowered to the measuring position and a humidity collar was added during the "sample trim" phase to prevent sample evaporation during the measurement. Frequency sweep experiments were performed at a strain amplitude of 0.1% strain and the angular frequency was ramped down from 100 rad/s to 1 rad/s. Strain amplitude sweep experiments were performed at an angular frequency of 10 rad/s and the strain amplitude was ramped up from 0.1% to 100% strain.

<u>Hydrogen Production Experiments:</u> Stock solutions of 10% functionalized polymer **2** and PMI CA **1** from  $\phi = 0$  to  $\phi = 1$  (9.6 mM of PMI chromophore, 50 mM aq. NaCl) were annealed by placing them in a 95°C water bath for 1 h then slow cooling the samples to room temperature over 18 h. Ascorbic acid stock solutions (1.7 M, 0.299 g/mL) were adjusted to pH 4 using 4 M NaOH<sub>(aq)</sub> (measured using a Fisher Scientific Accumet Research AR50 Dual Channel pH/Ion/Conductivity Meter, calibrated with pH 4.0 and pH 7.0 standard solutions). Samples were prepared by adding 100 µL of the PMI-functionalized polymer and PMI CA stock solution, 20 µL of a solution of the [Mo<sub>3</sub>S<sub>13</sub>]<sup>2-</sup> catalyst (180 µM, 1.00 mg in 7.5 mL), along with 860 µL of ascorbic acid solution (serving as a source of protons and sacrificial electrons) to a 9 mL screw cap vial with a silicone/PTFE septum. Vials were sealed and purged for 30 min with argon by using steel needles

as inlet (inserted through the cap inside the solution) and outlet (to the headspace). The pressure of Ar in the headspace was then equilibrated to 1 atm. Unless otherwise specified, the vials were then illuminated for 18 h using a homebuilt photoreactor made of white LEDs (Cree XLamp XT-E White LEDs 5000K, LEDsupply.com). The intensity of the white LEDs was evaluated at 447 nm LED at 250 W cm<sup>-2</sup>, measured using an optical power meter PM100D with optical sensor S120VC from Thorlabs) Each vial was suspended on top of a single LED, equipped with a lens, using a homebuilt sample holder. Analyses of gases evolved in the headspace during the photocatalysis were performed with a custom-built Shimadzu GC-2014 gas chromatography system equipped with a thermal conductivity detector. H<sub>2</sub> production was quantitatively detected using HayeSep T (1/16 inch, 7.5 m) and MS-5A (1/16", 2.5 m) columns. Temperature was held at 100°C for the detector and 40°C for the oven. The carrier gas was argon flowing at 8.5 mL/min, at constant pressure of 3.7–3.8 bars. Injection was performed via an autosampler equipped with a gas-tight (1000 µL, SGE) syringe. Calibration curve for H<sub>2</sub> was performed by injecting known quantities of 1% mol H<sub>2</sub> standard and pure H<sub>2</sub> gas. Experiments were performed at least in triplicate. The photocatalytic performance over time was evaluated by taking 250 µL of headspace from each vial, every 18 h, and analyze its contents on the GC. This was repeated for a total of seven times (5 days or 126 h of total irradiation).

## **Supplementary Text**

<u>Analytical Theory of Nanostructure Morphology:</u> We analytically calculate the optimal aspect ratio of the nanostructures by considering the competition between crystal formation and polymerbackbone repulsion. To this end, we consider the balance of two thermodynamic forces: the free energy penalty of polymer confinement and the line tension of the nanostructure. Polymers can wrap around the edges of the nanostructure and the space around these edges provides additional volume available to polymers. Hence, the surface density of the polymers is lower for narrow nanostructures. On the other hand, line tension tends to reduce the total edge length, thus preferring wide structures. In the following we estimate the two thermodynamic contributions and calculate how the co-assembly ratio affects the equilibrium morphology.

The configuration of the polymer on the nanostructure consists of a series of loops with the mean loop size determined by the functionalization of the polymer. The standard Flory–Huggins mean-field theory <sup>17</sup> predicts the free energy density per polymer segment,

$$f_{\rm FH} = k_{\rm B}T\left(\frac{\theta}{N}\log(\theta) + (1-\theta)\log(1-\theta) + \chi\theta(1-\theta)\right)$$
(S1)

with  $k_BT$  the thermal energy,  $\theta$  the volume fraction of the polymer and  $\chi$  the Flory interaction parameter. *N* is the number of segments per polymer determined by the polymer molecular weight; in the following we assume that *N* is large and that the first term in Eq. S1 is negligible. We apply this free-energy-density function to the covalent polymer wrapped around the nanostructure as shown in Figure S34a. Any results are expected to be at most semi-quantitatively accurate due to approximations applied; we treat the wrapped polymer as a mean-field solution and neglect the electrostatic effects of the charged polymer as well as effects due to finite persistence length and confinement to the surface. The simple theory can, however, predict trends and provide an intuitive explanation for the observed morphologies of the nanostructures. To calculate the polymer volume fraction  $\theta$  we need to restrict the geometry of the nanostructures. Guided by experimental results the nanostructure is assumed to be of rectangular shape with width A and length B shown in Figure S34a. The total volume occupied by the polymers is thus  $V_p = \frac{AB\phi}{abf}s\sigma$ , with  $\phi$  the co-assembly ratio, f the functionalization, a and b the single chromophore dimensions, s the cross-sectional area of the polymer chain and  $\sigma$  the monomer size, i.e., the distance between attached chromophores on the chain at maximum functionalization (f = 1). The polymer is confined to the surface of the nanostructure, but can also wrap around the edges as shown in Figure S34. The total volume available to the polymer is thus composed of the two surfaces and the four edges,  $V = 2AB\delta + 2(h + 2\delta)\delta(A + B)$ ), with h is the edge thickness and  $\delta$  the effective distance normal to the surface within which the polymer is confined. We approximate the polymer mean-field density distribution as Heaviside step function normal to the nanostructure surface. The volume fraction of the covalent polymers then becomes

$$\theta = \frac{V_{\rm p}}{V} = \frac{\phi\sigma s}{2abf\delta(1 + (h + 2\delta)(A^{-1} + B^{-1}))}$$
(S2)

In addition, the crystalline lattice of the chromophores gives rise to a line tension along the edges of the rectangular nanostructure. The line tensions  $\gamma_A$  and  $\gamma_B$  determine the equilibrium aspect ratio of the nanostructure when no covalent polymers are present ( $\phi = 1$ ).

Thus, the total free energy of the nanostructure is obtained by summing the line tension and polymeric contributions,

$$F(A,B) = 2A\gamma_{\rm A} + 2B\gamma_{\rm B} + f_{\rm FH}\frac{V}{s^{3/2}}$$
(S3)

where the volume of a single polymer segment is assumed to be  $s^{3/2}$ . Since  $f_{\text{FH}}$  is a free energy density per polymer segment, Eq. S1, a factor  $\frac{V}{s^{3/2}}$  is required to obtain the total polymer free energy. Minimizing this free energy yields the equilibrium size of the nanostructure. Under conditions when the amount of material (i.e., PMI molecules) is limited the surface area is constant, AB = S = const. The width of the nanostructure is obtained by minimization,  $\frac{\partial F(A,S/A)}{\partial A} = 0$ , and the aspect ratio is  $\alpha = B/A$ . On the other hand, when the amount of available material is infinite, the length of the nanostructure also tends to infinity and the width of the structure is obtained by solving  $\frac{\partial F(A,B\to\infty)}{\partial A} = 0$ .

The solution will depend on the parameters in Eq. S2 and these parameters can be estimated from the molecular structure of the polymer and the chromophore molecule. The polymer cross-section is about 0.9 nm × 0.5 nm or s = 0.4 nm<sup>2</sup>, the monomer size  $\sigma = 0.4$  nm, the chromophore dimensions a = 0.84 nm and b = 0.35 nm, and the edge length is approximately one chromophore length h = 1 nm. Estimating the confining distance of the polymer to the surface is somewhat more involved, and the estimate will in principle depend on the persistence length and the functionalization. The polymer configuration can be pictured as a series of loops of average length  $\overline{l} = \sigma/f$ . For the polymer under study this length is similar to the persistence length, so that standard scaling theory for flexible polymers <sup>18</sup> cannot be used. Furthermore, we expect that

polymers are functionalized uniformly and randomly, implying an exponential distribution of loop lengths. The scaling theory of de Gennes for adsorbed polymers results in a power-law distribution and cannot be used in our case, where the loop size distribution is predetermined by the polymer functionalization <sup>18</sup>. We observe that the polymer conformation can be statistically described by the worm-like chain model <sup>17</sup>, where equipartition theory assigns each flexural mode (Fourier space mode) an average energy of  $1k_{\rm B}T$ . For the parameters considered in this work the loop lengths are comparable to, or shorter than, the persistence length of the polymer. Therefore, we approximate the flexural fluctuations by considering only the dominant lowest order flexural mode. The curvature energy of a polymer is a contour integral of the curvature C:  $E_c =$  $\frac{k_{\rm B}Tl_{\rm p}}{2}\int_0^l C^2 dx$ . The height of a circular arc of radius R = 1/C is  $y = R\left(1 - \cos\left(\frac{l}{2R}\right)\right) \approx \frac{l^2}{8R}$  to second-order Taylor expansion. The curvature energy of such an arc is  $E_c = \frac{k_B T l_p l}{2R^2}$ . Assuming that  $E_{\rm c} = k_{\rm B}T$  we obtain the loop height  $y(l) \approx \frac{\sqrt{2} l^{3/2}}{8\sqrt{l_{\rm p}}}$ . Moreover, averaging over an exponential loop size distribution  $p(l) = \frac{1}{\bar{l}}e^{-l/\bar{l}}$  we find  $\bar{y}(\bar{l}) \approx \frac{3\sqrt{2\pi}\,\bar{l}^{3/2}}{32\sqrt{l_p}}$ . The persistence length of the polymer is  $l_{\rm p} = 7$  nm. At functionalization f = 0.1 the mean loop size is  $\bar{l} = \frac{\sigma}{f} = 4$  nm and the mean loop height is  $\bar{y} = 0.7$  nm. As noted above, this derivation is valid for relatively stiff loops,  $y < \frac{l}{\pi}$ , which implies  $\bar{l} < 2l_p$ . Hence, for the polymer used in this work ( $l_p = 7 \text{ nm}$ ) the theory is valid at sufficiently large functionalization,  $f > \frac{\sigma}{2l_n} \approx 0.03$ . Moreover, the theory assumes that the polymers are able to wrap around the edges, necessitating a sufficiently long loop length,  $l_m >$  $\frac{\pi h}{2}$ . The probability to obtain such a loop is  $p(l > l_m) = e^{-l_m/\bar{l}}$ . A reasonable fraction of all loops must be sufficiently long to enable edge-wrapping of the polymers. We set  $p(l > l_m) = 0.1$ , which limits the functionalization at which the theory is expected to be valid to about f < 0.6.

Since the polymer cross-sectional area is *s*, a distance  $\sqrt{s}$  perpendicular to the nanostructure must be accessible even in the limit of stiff polymers, in which case the problem reduces to an equivalent 2D polymer problem. Furthermore, polymers are attached to the chromophore via a  $\delta_l \approx 0.8$ nm long flexible linker. The total window accessible to the polymer is thus

$$\delta = \delta_l + \bar{y} + \sqrt{s} = \delta_l + \sqrt{s} + \frac{3\sqrt{2\pi}\,\bar{l}^{3/2}}{32\sqrt{l_p}} \tag{S4}$$

resulting in distance about of about  $\delta \sim 2$  nm at f = 0.1. The line tension is estimated from the dimerization free energy of the chromophore molecules  $\Delta G = -18k_{\rm B}T^{11}$  which results in  $\gamma_{\rm A} \approx -\frac{\Delta G}{a} \approx 20k_{\rm B}T/\text{nm}$  and the edge line tension from the aspect ratio  $\alpha \sim 5$  when no polymers are present:  $\gamma_{\rm B} = \frac{\gamma_{\rm A}}{\alpha} = 4k_{\rm B}T/\text{nm}$ . Finally, the Flory parameter  $\chi$  is the only parameter we are unable to determine. Since no phase segregation in the polymer density is observed we deduce that  $\chi < 1/2$ . In the following we shall assume  $\chi = 0$ , but we stress that the results do not change qualitatively when varying the Flory parameter within reasonable bounds, i.e.,  $-1 < \chi < 1/2$ .

The theoretically predicted width and aspect ratio of the nanostructure are shown in Figure S35. The results demonstrate that the width of the nanostructures increases with increasing co-assembly

ratio (i.e., the fraction free chromophores not attached to the covalent polymer), while the aspect ratio decreases. Varying the Flory parameter  $\chi$  has an effect similar to varying the functionalization, thereby changing the total mass of covalent polymer in the structure. The trend and magnitude of the values agreed with experimental data, cf. Figures 3i) and 3k) in the main text. We conclude that the morphology of the nanostructures is largely determined by the balance of thermodynamic forces, i.e., the line tension and the polymer pressure. However, polymers wrapped around the edges can affect the kinetics of growth by impeding the lateral growth of the nanostructures and the size of nanostructures is affected by the local availability of material, i.e., diffusion and attachment/detachment dynamics during the annealing process. At high values of  $\phi$ , the equilibrium width of the nanostructures increases without bounds (Figure S35a) to minimize the line tension. We hypothesize that the finite size observed in experiments is due to limitations in kinetics and diffusion and the local availability of material. These effects can be approximately accounted for by restricting the size of the nanostructure, see Figures S35a and Figure S35b.

Within the range of theory validity, 0.03 < f < 0.6, increasing the polymer functionalization reduces the aspect ratio, see Figure S35d,f. The theory predicts no dependence on the polymer molecular weight as long as the polymers are sufficiently long (Eq. S2) agreeing with the simulation results in Figure S30.

The experimentally determined size of a single nanostructure is about  $S = 5 \cdot 10^4$  nm<sup>2</sup>. Figure S36 shows the comparison between the theoretical prediction and experimental results for the aspect ratio at functionalization f = 0.1. The equilibrium theory captures the trend and matches the experimental results at high co-assembly ratios. However, at low co-assembly ratios the theory predicts about an order of magnitude larger aspect ratio. We speculate that the discrepancy is mainly due to the artefacts of sample preparation when imaging the samples under TEM. For example, the sedimentation of the nanostructures on the TEM grids can result in the breaking of nanostructures, thus lowering the observed aspect ratio. Experimentally measuring the aspect ratio of high aspect ratio objects is also biased towards lower aspect ratios, since it is easier to find fiber ends for shorter fibers. Furthermore, the finite speed of the annealing process limits the maximum size of the structures that are expected to form. Hence, the equilibrium theory prediction can be regarded as an upper bound for the aspect ratio of the nanostructure in solution, which would be attained after an infinitely slow annealing process.



Figure S1. Chemical structures and names of compounds used in this study.



Figure S2. Scheme for the synthetic procedure of compound 6.



Figure S3. General procedure to synthesize polymer 2 by functionalizing PEAMA.



**Figure S4.** <sup>1</sup>H NMR spectra (500 MHz, DMSO- $d_6$ ) of polymer **2** at different degrees of PMI functionalization with labeled protons from the polymer backbone and the chromophore functional group. A few microliters of deuterated trifluoroacetic acid were added to the solutions to help solubilize polymer **2**.



**Figure S5.** Absorption spectra (left) and corresponding Beer's law calibration curve (right) to calculate the molar absorptivity of the PMI chromophore (CA 1) in DMSO. The molar absorptivity was used to calculate the percent functionalization of PEAMA from the absorbance spectra of PMI functionalized polymer in DMSO. Representative spectra are shown in Figure S6. Absorption spectra were measured using a 1 cm path length cuvette.



**Figure S6.** Absorption (a) and fluorescence (b) spectra of PMI-functionalized polymers at different percent functionalization in DMSO. Absorption (c) and emission (d) spectra of PMI-functionalized polymers at different percent functionalization in 50 mM  $NaCl_{(aq)}$ . Emission spectra were taken at the iso-absorbance point for all samples with an excitation wavelength of 420 nm.



**Figure S7.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 1% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S8.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 5% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S9.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 10% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



Figure S10. Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 15% functionalized polymer 2 and CA 1 from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S11.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 20% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S12.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 25% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S13.** Comparative plots of SAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 30% functionalized polymer **2** and CA **1** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively. X-ray scattering measurements were performed in satic capillaries.



Figure S14. 2D WAXS patterns for the co-assembly of 30% functionalized polymer 2 and CA 1 from  $\phi = 0$  to  $\phi = 0.9$ .



Figure S15. Phase diagram for the co-assembly of polymer 2 and CA 1 at different polymer functionalization and co-assembly ratios. The regions of the plot corresponding to the  $\alpha$ -phase mixture,  $\beta$ -phase, and the mixed  $\alpha/\beta$  two-phase region are colored in blue, red, and yellow, respectively, and assigned based on the UV–Vis spectra and WAXS patterns.



**Figure S16.** Conventional TEM micrographs of 10% (a) and 20% functionalized (b) polymer **2** stained with a 1 wt% UA solution.



Figure S17. Phase diagram for the co-assembly of polymer 2 and CA 3 at different polymer functionalization and co-assembly ratios. The regions of the plot corresponding to the amorphous/ $\alpha$ -phase mixture,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively, and assigned by the UV–Vis spectra and WAXS patterns.



**Figure S18.** Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 1% functionalized polymer **2** and CA **3** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed static capillaries.



**Figure S19.** Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 5% functionalized polymer **2** and CA **3** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S20.** Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 10% functionalized polymer **2** and CA **3** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed in static capillaries.



Figure S21. Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 15% functionalized polymer 2 and CA 3 from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed in static capillaries.


**Figure S22.** Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 20% functionalized polymer **1** and CA **3** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed in static capillaries.



Figure S23. Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 25% functionalized polymer 2 and CA 3 from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan and purple, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S24.** Comparative plots of the MAXS, WAXS and UV–Vis absorption spectroscopy data for the co-assembly of 30% functionalized polymer **2** and CA **3** from  $\phi = 0$  to  $\phi = 1$ . The regions of the plot corresponding to the  $\alpha$ -phase,  $\gamma$ -phase, and the mixed  $\alpha/\gamma$  two-phase regions are colored in blue, cyan, and purple, respectively. X-ray scattering measurements were performed in static capillaries.



**Figure S25.** Analysis of WAXS for polymer **2** and CA **3** from  $\phi = 0$  to  $\phi = 1$ , showing full width at half max (FWHM) of the  $\pi$ - $\pi$  stacking peaks at q = 0.83 Å<sup>-1</sup> (error bars denote  $\pm$  standard deviation across the full range of functionalization ratios). The decrease in FWHM indicates that the crystal domain size of the polymer crystal phase is increasing upon addition of CA.



Figure S26. (a) WAXS patterns comparing the crystallization of CA 1 with and without the presence of 0%-functionalized polymer 2 (i.e., poly(ethylene-*alt*-maleic acid). (b) WAXS patterns comparing the crystallization of CA 3 with and without the presence of 0%-functionalized polymer 2 (i.e., poly(ethylene-*alt*-maleic acid). In (a) and (b), the decrease in peak intensity for samples containing 0%-functionalized polymer 2 is due to the lower concentration of chromophore or possible increase in amorphous content.



**Figure S27.** Conventional TEM micrographs of 10% functionalized polymer 2 and CA 1 at  $\phi = 0.1$  (a),  $\phi = 0.2$  (b),  $\phi = 0.3$  (c),  $\phi = 0.4$  (d),  $\phi = 0.5$  (e),  $\phi = 0.6$  (f),  $\phi = 0.7$  (g),  $\phi = 0.8$  (h), and  $\phi = 0.9$  (i). Samples are stained with a 1 wt% UA solution.



Figure S28. Cryo-TEM micrographs of 30% functionalized polymer 2 and CA 1 at  $\phi = 0$  (a),  $\phi = 0.2$  (b),  $\phi = 0.4$  (c),  $\phi = 0.6$  (d), and  $\phi = 0.8$  (e).



**Figure S29.** Chromophore PMI model. (a) Molecular structure with experimental values for the dimensions obtained from a single crystal structure<sup>19</sup> and the dipole moment obtained from DFT calculations. (b) Coarse grained model: Each sphere is described by a Lennard–Jones 12–6 potential and the entire chromophore (consisting of green, pink, and red spheres) is a rigid body. The four red spheres are charged positively (bottom) and negatively (top) with  $q = \pm 0.1q_0$  to accurately capture the electrostatic dipole, quadrupole and octupole moments of the chromophore molecule. The purple sphere represents the charged tail and is connected with the chromophore via a harmonic bond. The interactions are described in Table S3.



**Figure S30.** Morphology of the nanostructures dependence on the co-assembly ratio  $\phi$ . (a,b) Resulting structures after annealing obtained from MD simulations for  $\phi = 0$  to  $\phi = 1$  in increments of 0.1 for low molecular weight polymer with 30 beads per polymer (a) and high molecular weight polymer with 150 beads per polymer (b) at f = 0.3. Some of the structures in (a) are also show in in Figure 3 in the main text. (c) Aspect ratio of the structures in (a) and (b) calculated from Eq. S1. Simulation parameters: N = 500 chromophores,  $l_p = 20\sigma$ .



**Figure S31.** Mixing parameter for the structures shown in Figure S30a and in main text Figure 3. The parameter  $S_m = N_{unlike}/2N\phi(1 - \phi)$  is calculated by enumerating all unlike neighbors (chromophores attached to the backbone, colored blue in the main text Figure 3) of all free chromophores (not attached to the backbone, colored red)  $N_{unlike}$ , and dividing by the number of such neighbors expected by ideal mixing,  $N_{unlike,ideal}=2N\phi(1-\phi)$ . N s the total number of neighbors and  $r_c$  is the cut-off used for the neighbor definition;  $r_c = 2\sigma$  captures only nearest neighbors, whereas  $r_c = 3\sigma$  also captures next-nearest neighbors. The cut-off is calculated from the center-of-mass positions of the chromophores. The mixing parameter is close to unity, indicating that covalent and supramolecular polymers are well mixed.



**Figure S32.** Principal components of the radius of gyration tensor corresponding to the configurations in Figure S30. (a) Low molecular weight and (b) high molecular weight polymer. Gyration tensor eigenvalues are calculated for each polymer backbone, ordered from smallest ( $r_{g1}$ ) to largest ( $r_{g3}$ ), and averaged over all polymers in the system. For reference, the dotted lines correspond to the gyration eigenvalues obtained at high temperature ( $T^{high} = 3T$ ), where the structures disassemble.



**Figure S33.** Effect of changing the polymer persistence lengths  $l_p$ . (a-d) Final configurations after simulated annealing at  $\phi = 0.3$  and (a)  $l_p = \sigma$ , (b)  $l_p = 10\sigma$ , (c)  $l_p = 20\sigma$  and (d)  $l_p = 100\sigma$ . (e) Nanostructure aspect ratio increases slightly with increasing persistence length, but the effect is small. Co-assembly occurred for all simulated persistence lengths. However, intermediate persistence lengths appear to have resulted in the largest ordered domain sizes (c). At small persistence lengths (a,b) individual chains easily fold onto themselves which hampers the coassembly process, whereas at large persistence lengths the high bending energy hinders coassembly into ordered domains and results in a branched structure (d). Parameters: N = 500, functionalization f = 0.3 and molecular weight  $M_w = 30$  beads.



**Figure S34.** Schematic model of the nanostructure. (a) Schematic of the nanostructure of width *A* and length *B*. The chromophore 2D crystal is colored red and the covalent polymer is shown in blue. (b) Mean-field approximation where polymers are able to occupy all space within a distance  $\delta$  around the 2D crystalline structure of width *A* and thickness *h*.



**Figure S35.** Results of the analytical theory. The left panels (a,c,e) show the nanostructure width and the right panels (b,d,f) show the aspect ratio as a function of the co-assembly ratio. The reference curve (black) is obtained at  $S = 10^4$  nm<sup>2</sup>,  $\chi = 0, f = 0.1$ . The top two panel (a,b) show the effect of varying the total surface area of the nanostructure *S*, the middle two panels (c,d) show the effect of the Flory parameter  $\chi$  and the bottom two panels (e,f) show the effect of functionalization *f*.



**Figure S36.** Comparison between analytical theory (blue curve) and experimental results (red circles) at functionalization f = 0.1. The calculation assumed constant size of the nanostructure  $S = 104 \text{ nm}^2$  and Flory parameter  $\chi = 0$ .



**Figure S37.** Variable temperature wide-angle x-ray scattering (VT-WAXS) patterns for the formation of the  $\phi = 0.1$ ,  $\phi = 0.2$ ,  $\phi = 0.3$ ,  $\phi = 0.4$ , and  $\phi = 0.5$ . X-ray scattering measurements were performed in a static capillary.



**Figure S38.** Variable temperature wide-angle x-ray scattering (VT-WAXS) patterns for the formation of the  $\phi = 0.6$ ,  $\phi = 0.7$ ,  $\phi = 0.8$ ,  $\phi = 0.9$ , and  $\phi = 1.0$ . X-ray scattering measurements were performed in a static capillary.



**Figure S39.** (a) The degree of conversion of the  $\beta$ -phase to the melted, amorphous phase as monitored by the normalized absorbance intensity of the 440 nm and 570 nm peaks in the absorption spectrum of CA 1 that are associated with the crystalline  $\beta$ -phase. (b) Absorption spectra for the melting of the CA 1  $\beta$ -phase into an amorphous phase. Spectra over time are colored from red (t = 0 min) to gray (t = 60 min) with the arrows indicating the peak changes over time. Measurements were performed at a fixed temperature of 95°C.



**Figure S40.** (a) The degree of conversion for different phases as monitored by the normalized absorbance intensity of the 430 nm peak (associated with the  $\alpha$ -phase crystal structure) and the 570 nm peak (associated with the  $\beta$ -phase crystal structure) for a system at  $\phi = 0.3$ . (b) Absorbance spectra for the formation of the hybrid bonding polymer at  $\phi = 0.3$ . Spectra over time are colored from red (t = 0 min) to blue (t = 60 min) with the arrows indicating the peak changes over time. (c-d) Zoomed in spectra from panel b for the region associated with  $\alpha$ -phase growth (c) and  $\beta$ -phase melting (d). Measurements were performed at a fixed temperature of 95°C over one hour.



**Figure S41.** AFM micrographs of a 10% functionalized polymer 2 at  $\phi = 0.5$ . Marked locations indicate areas where AFM indentation and fracture tests were performed.



**Figure S42.** Force versus separation curves for the AFM nanoindentation and fracture tests from Figure S41. The approach part of each force curve is labeled in blue and the retracting part is labeled in red. The inflection point of the approach curve indicating fracture is labeled by the dashed red line.



**Figure S43.** AFM micrographs of a 10% functionalized polymer **2** at  $\phi = 0.8$ . Marked locations indicate areas where AFM indentation and fracture tests were performed.



**Figure S44.** Force versus separation curves for the AFM nanoindentation and fracture tests from Figure S43. The approach part of each force curve is labeled in blue and the retracting part is labeled in red. The inflection point of the approach curve indicating fracture is labeled by the dashed red line.



**Figure S45.** AFM micrographs of a PMI CA 1 ( $\phi = 1.0$ ). Marked locations indicate areas where AFM indentation and fracture tests were performed.



**Figure S46.** Force versus separation curves for the AFM nanoindentation and fracture tests from Figure S45.The approach part of each force curve is labeled in blue and the retracting part is labeled in red. The inflection point of the approach curve indicating fracture is labeled by the dashed red line.



**Figure S47.** Healing of the structures after repeated indentations for  $\phi = 1.0$  (dark blue),  $\phi = 0.8$  (red) and  $\phi = 0.5$  (light blue). The square, circle and triangular symbols designate different waiting times between repeated indentation events. No healing is observed at  $\phi = 1.0$ , while structures with lower  $\phi$  exhibit partial recovery of the material and the material is repeatedly fractured on subsequent indentation events.



**Figure S48.** AFM indentation force curves for 6 repeated indentation events at three different waiting times between indentations: (a) 30 s, (b) 60 s, and (c) 300 s at  $\phi = 1$ . The locations on the nanostructure (d) marked by (1,2,3), respectively, show the locations where each of the (a,b,c) indentation sets were performed. The final AFM image of the nanostructure after the final indentation step (e) shows that small holes are present, indicating that structures did not heal.



**Figure S49.** AFM indentation force curves for six repeated indentation events at three different waiting times between indentations: (a) 30 s, (b) 60 s, and (c) 300 s at  $\phi = 0.8$ . The locations on the nanostructure (d) marked by (1,2,3), respectively, show the locations where each of the (a,b,c) indentation sets were performed. (e) AFM image of the nanostructure after the final indentation step.



**Figure S50.** AFM indentation force curves for six repeated indentation events at three different waiting times between indentations: (a) 30 s, (b) 60 s, and (c) 300 s at  $\phi = 0.5$ . The locations on the nanostructure (d) marked by (1,2,3), respectively, show the locations where each of the (a,b,c) indentation sets were performed. (e) AFM image of the nanostructure after the final indentation step.



**Figure S51.** Shear force response of the structures. (a) Schematic of the initial setup. The left part of the structure, colored orange, is immobilized (schematically shown by a gray-colored clamp). Force is applied in the *y*-direction to the right side of the structure, also colored orange. (b) Shear force curves corresponding to structures at various co-assembly ratios  $\phi$ . The structures at  $\phi = 0.3$  and  $\phi = 0.7$  are shown in the main text Figures 3 and 5. The yield point at the rightmost end of each curve is marked by **x**. (c) Yield force as a function of  $\phi$  for the full structures (black) and the same structures with the covalent polymer backbone removed (red).



**Figure S52.** Stress distribution under increasing shear force at  $\phi = 0.8$ : a)  $f_{xy} = 15k_BT/\sigma$ , b)  $f_{xy} = 33k_BT/\sigma$ , c)  $f_{xy} = 75k_BT/\sigma$  and d)  $f_{xy} = 210k_BT/\sigma$ . The left part of the structure, colored grey, is clamped (immobilized) and a force  $f_{xy}$  is applied to the right part of the structure (colored grey). The middle section of the crystal is color-coded according to the trace of the stress tensor of individual chromophores, i.e., the local pressure *p* from dark red ( $p = -20k_BT/\sigma^3$ ) to dark blue ( $p = 20k_BT/\sigma^3$ ). Moderate shear stress leads to crystal lattice breaking due to stress localization (a), while polymer backbones (blue) prevent full fracture (b). Due to multiple attachment points of each polymer, the stress transmitted by the polymers is delocalized (c, d), thus preventing full breakage even under very high applied force.



**Figure S53.** Crystal healing at  $\phi = 0.8$ . The starting structure (a) is placed under simultaneous shear force  $f_{xy}$  and extension force  $f_{xx} = f_{xy} = 20k_{\rm B}T/\sigma$ , leading to breaking of the crystal (b). Subsequently the force is removed,  $f_{xx} = f_{xy} = 0$ , and the structure begins to spontaneously heal (c). After time  $t = 10^4 \tau$  the crystal is almost completely healed (d), although residual stress remains due to dislocation defects, which would require more time to spontaneously relax. The stress distribution in the crystal is shown using the red (expansion stress) to blue (compressive stress) color scale showing the trace of the stress tensor of individual chromophores.



**Figure S54.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0$ . UV–Vis absorption spectrum (right) shows that the  $\alpha$ -phase crystal structure is preserved after gelation.



**Figure S55.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.1$ . UV–Vis absorption spectrum (right) shows that the  $\alpha$ -phase crystal structure is preserved after gelation.



**Figure S56.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.2$ . UV–Vis absorption spectrum (right) shows that the  $\alpha$ -phase crystal structure is preserved after gelation.



**Figure S57.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.3$ . UV–Vis absorption spectrum (right) shows that the  $\alpha$ -phase crystal structure is preserved after gelation.



**Figure S58**. Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.4$ . UV–Vis absorption spectrum (right) shows that the mixed  $\alpha/\beta$ -phase crystal structure is preserved after gelation.



**Figure S59.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.5$ . UV–Vis absorption spectrum (right) shows that the mixed  $\alpha/\beta$ -phase crystal structure is preserved after gelation.



**Figure S60.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.6$ . UV–Vis absorption spectrum (right) shows that the mixed  $\alpha/\beta$ -phase crystal structure is preserved after gelation.



**Figure S61.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.7$ . UV–Vis absorption spectrum (right) shows that the  $\beta$ -phase crystal structure is preserved after gelation.



**Figure S62.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.8$ . UV–Vis absorption spectrum (right) shows that the  $\beta$ -phase crystal structure is preserved after gelation.



**Figure S63.** Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 0.9$ . UV–Vis absorption spectrum (right) shows that the  $\beta$ -phase crystal structure is preserved after gelation.



Figure S64. Representative frequency sweep (left) and amplitude sweep (middle) curves for rheological properties of the crosslinked gels at  $\phi = 1.0$ . UV–Vis absorption spectrum (right) shows that the  $\beta$ -phase crystal structure is preserved after gelation.


**Figure S65.** (a) UV–Vis absorption spectra of catalysis solutions containing polymer **2** at 10% functionalization and CA 1 from  $\phi = 0$  to  $\phi = 0.8$ . All spectra show the characteristic crystalline absorbance peak that is indicative of charge-transfer exciton formation and match well with the WAXS and UV–Vis absorption spectroscopy data in Figure S9. (b) Turnover numbers (TON) of hydrogen produced with a thiomolybdate catalyst as a function of  $\phi$  for hybrid bonding polymers formed between polymer **2** at 10% functionalization and CA 1. Error bars denote  $\pm$  standard deviation.



**Figure S66.** Representative photographs of the samples containing 10% functionalized polymer 2 and PMI CA 1 from  $\phi = 0$  to  $\phi = 1$  used for the H<sub>2</sub> production experiments. The chromophore assemblies remain solubilized in the catalysis solution at pH 4 for co-assembly ratios from  $\phi = 0$  to  $\phi = 0.8$ ; however, the assemblies precipitate from solution at co-assembly ratios from  $\phi = 0.9$  and  $\phi = 1.0$ .

Polymer Batch	Peak Ratio (β)	% Func. (NMR)	% Func. (UV–Vis.)
1%-functionalized polymer 2	0.029	1.2	0.88
5%-functionalized polymer 2	0.11	4.7	4.34
10%-functionalized polymer 2	0.21	9.6	7.93
15%-functionalized polymer 2	0.28	14	13.45
20%-functionalized polymer 2	0.37	19	17.55
25%-functionalized polymer 2	0.43	23	23.50
30%-functionalized polymer 2	0.55	33	27.75

**Table S1.** PMI-functionalization of PEAMA versus the experimental PMI-functionalization of PEAMA as measured with <sup>1</sup>H NMR and UV–Vis absorption spectroscopy.

Sample	PMI Conc. (mM)	wt%	рН
CA 1	5	0.23	7.52
0%-functionalized polymer 2	N.A.	2.83	8.01
1%-functionalized polymer 2	1.25	2.13	6.81
5%-functionalized polymer 2	5	1.41	7.26
10%-functionalized polymer 2	5	0.78	7.15
15%-functionalized polymer 2	5	0.57	7.20
20%-functionalized polymer 2	5	0.47	7.28
25%-functionalized polymer 2	5	0.41	7.12
30%-functionalized polymer 2	5	0.36	7.02
CA <b>3</b>	5	0.26	7.83

Table S2. Conditions for the co-crystallization of covalent polymer 2 with both CA 1 and CA 3

Bead Type	Pink	Green	Red	Purple
Pink	LJ ( $\varepsilon_{\pi}, r_{c} = 3.5\sigma$ )	LJ ( $\varepsilon_{\rm rep}$ , $r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )
Green	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm hf}$ , $r_{\rm c}$ =3.5 $\sigma$ )	LJ ( $\varepsilon_{\rm hf}$ , $r_{\rm c}$ =3.5 $\sigma$ )	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )
Red	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm hf}$ , $r_{\rm c}$ =3.5 $\sigma$ )	LJ ( $\varepsilon_{\rm hf}$ , $r_{\rm c}$ =3.5 $\sigma$ )	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )
			Coul $(0.1q_0, \epsilon_r = 1)$	
Purple	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm rep}, r_{\rm c} = 2^{1/6} \sigma$ )	LJ ( $\varepsilon_{\rm rep}$ , $r_{\rm c} = 2^{1/6} \sigma$ )	Yukawa $(q_0, \varepsilon_r = 80, l_D = 4\sigma)$

**Table S3.** Interaction matrix between different beads of the coarse-grained model depicted in Figure S28. "LJ" denotes the shifted-and-truncated Lennard–Jones interaction, "Coul" denotes the direct Coulombic interaction and "Yukawa" is used for the screened electrostatic repulsion between the charged tails.

**Movie S1** | Fracture behavior of the co-assembled HBP nanostructure under shear. As the shear force is linearly increased from  $f_{xy} = 0$  to  $f_{xy} = 250k_BT/\sigma$ , with molecular thickness  $\sigma = 3.2$  Å, the crystal lattice breaks while the covalent backbone (blue) maintains connectivity and significantly delays full fracture of the nanostructure. The clamped section of the structure is colored in grey and a force  $f_{xy}$  in the direction of the *y*-axis is applied to the right-hand section of the nanostructure (also colored grey), whereas the non-clamped region is colored according to the local stress, from red (tensile stress) to blue (compressive stress).

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