Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

for

Shape-Tunable Two-Dimensional Assemblies from Chromophore-Conjugated Crystallizable Poly(L-lactides) with Chain-Length-Dependent Photophysical Properties

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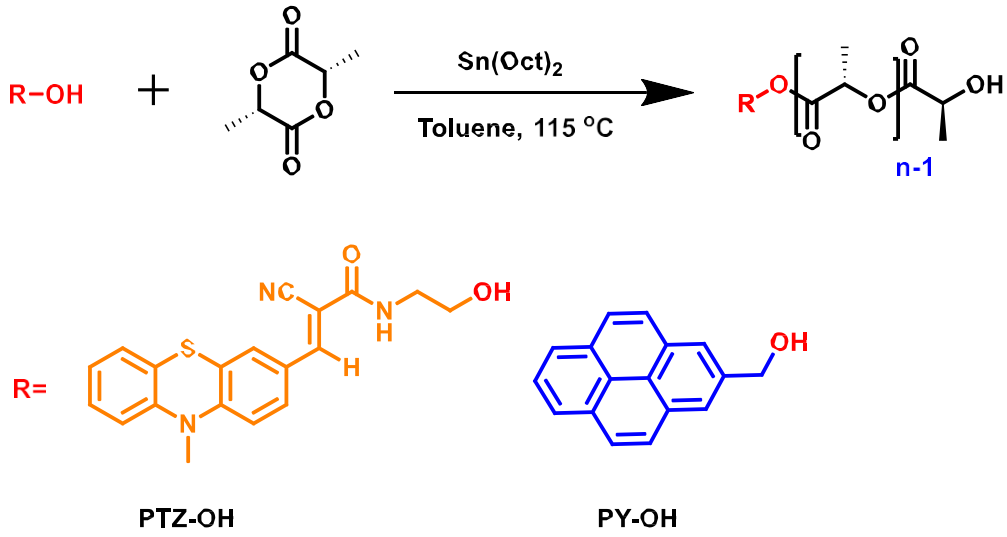
Materials and Methods

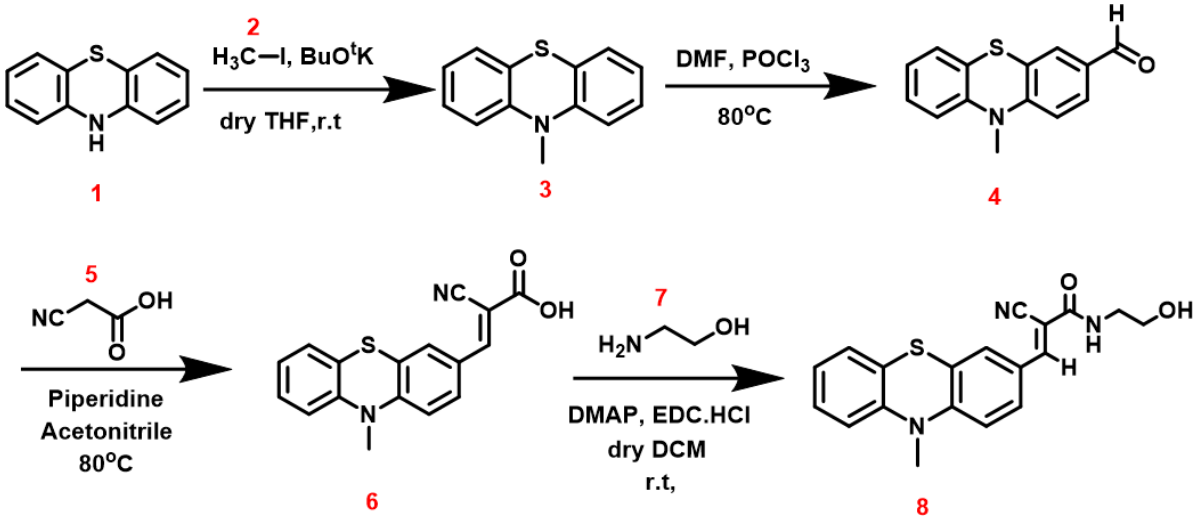
All chemicals were purchased from commercial suppliers, and no further purification was performed unless otherwise specified. Dried solvents for polymerization were purchased from Sigma Aldrich. ^{1}H-NMR spectra were measured on a Bruker 400 MHz NMR spectrometer using $CDCl_3$ and DMSO-D_6 as solvents. Chemical shifts (δ) are reported in ppm units with TMS as the internal standard. The coupling constant (J) is reported in hertz (Hz). Column chromatography was carried out on silica gel (100-200 mesh). Spectroscopic grade solvents were used for UV-Vis studies. UV-Vis spectra were recorded in a JASCO V-750 spectrophotometer. AFM imaging was performed in Asylum Research MFP-3D. Fluorescence spectra were recorded in a FluoroMax-3 spectrophotometer from Horiba Jobin Yvon. Time-correlated single photon counting (TCSPC) spectra measurements were done using a Horiba Delta flex-01 TCSPC spectrometer. The molecular weight of the polymers was determined by the end-group analysis from ^{1}H NMR and UV-Vis spectra. Molecular weight and dispersity ($Đ$) of the polymers were also estimated from size exclusion chromatography (SEC) at 30 °C using a Waters machine equipped with a 515 HPLC pump, Waters 2414 RI detector, and HSP gel HT 4.0/HSP gel HT 2.5 columns connected in a series. THF was used as an eluent. The flow rate was maintained at 0.6 mL/min. Dynamic Light Scattering (DLS) measurements were recorded using the Malvern instrument. Confocal Laser Scanning Microscopy (CLSM) images were obtained from the Carl Zeiss-LSM880 machine. Transmission Electron Microscopy (TEM) was performed in a Jeol 2100 LaB6 transmission electron microscope operating at 200 kV voltage. AFM imaging was performed in Asylum Research MFP-3D Rigaku Smart Lab (40 kV, 110 mA) equipped with a 0D detector (HyPix-3000) (Cu Kα1 radiation, λ = 1.5406 Å, scan speed = 50°/min, step size = 0.010°) was used to collect PXRD data. Differential Scanning Calorimetry (DSC) studies were conducted in the TA instrument's Q2000 model with a scan rate of 10 ^{o}C per min.

Synthesis and Characterization

PY-OH was purchased from commercial sources and used without further purification. **PTZ-OH** was synthesized following the literature procedure. [1,2,3]



Scheme S1. Synthetic scheme for chromophore-appended poly(L-lactides) (PLLAs) by ring opening polymerization (ROP) of L-lactide monomer.



Scheme S2. Synthesis of **PTZ-OH** (compound **8**).

Synthesis of compound 3:[1] Phenothiazine (2.0 g, 10 mmol) and potassium tert-butoxide (1.4 g, 15 mmol) were dissolved in dry THF at 0 °C. After stirring for 20 min, methyl iodide (2 mL, 30 mmol) was added to the solution, and the mixture was stirred for 36 h at room temperature in an inert atmosphere. The reaction was quenched with water, and the resulting mixture was extracted with

CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated to dryness under vacuum. The crude was purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and 0.5% ethyl acetate in hexane as eluent to obtain the desired product **3** as a white crystalline solid (1.6 g, yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.14 (m, 4H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 3.38 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.00, 127.58, 127.31, 123.59, 122.61, 114.23, 35.45; HRMS (ESI): m/z calcd: 214.069 $[M+H]^+$, found: 214.0351 $[M+H]^+$.

Synthesis of compound 4:[1] Phosphoryl chloride ($POCl_3$, 1.1 mL, 11.52 mmol) was added dropwise to dry DMF (1.01 mL, 13.21 mmol) at 0 °C. Compound **3** (0.6 g, 2.81 mmol) was dissolved in dry DCM and added to that mixture, and the dark brown solution was stirred at 80 °C for 12 h in an inert atmosphere. A saturated $NaHCO_3$ solution was added to the reaction mixture, and the aqueous layer was extracted using CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated to dryness under vacuum. The crude was purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and 10% ethyl acetate in hexane as eluent to obtain the desired product **4** as a yellow crystalline solid (450 mg, yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.86-6.83 (m, 2H), 3.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.25, 151.21, 144.22, 131.30, 130.60, 128.07, 127.90, 127.43, 124.11, 123.76, 122.67, 114.90, 113.84, 35.95; HRMS (ESI): m/z calcd 242.0639 $[M+H]^+$, found 242.0101 $[M+H]^+$.

Synthesis of compound 6:[2] Compound **4** (0.4 g, 1.66 mmol) and cyanoacetic acid (568 mg, 6.64 mmol) (**5**) were dissolved in acetonitrile (10 mL), and then piperidine (750 mL) were added to the mixture. The solution was refluxed for 12 h in an inert atmosphere. After that, the solution was dried in vacua, and the crude was purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and 1% MeOH in CH_2Cl_2 as eluent to obtain the desired product **6** as dark red amorphous solid (380 mg, yield: 75%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.16 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.04-7.01 (m, 2H), 3.39 (s, 3H)$^-$; ^{13}C NMR (151 MHz, DMSO): δ 164.20, 153.13, 149.84, 143.97, 132.33, 129.08, 128.64, 127.46, 126.11, 124.15, 122.74, 121.39, 117.24, 115.96, 115.29, 100.24, 36.08; HRMS (ESI): *m/z* calcd. 309.0697 $[M + H]^+$, found 309.0323 $[M + H].^+$

Synthesis of compound 8:[2] Compound **6** (160 mg, 0.52 mmol) and Dimethylaminopyridine (DMAP) (320 mg, 5 mmol) were taken in dry CH_2Cl_2 and stirred for 15 minutes at 0 ^{o}C and subsequently, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl) (200 mg, 1.62 mmol) was added to the reaction mixture. After 30 minutes of stirring, ethanol amine (80 µL, 1.215 mmol) was

added to the reaction vessel and kept for stirring 48 h at room temperature in an inert atmosphere. After that, the solution was dried in vacua, and the crude was purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and 20% ethyl acetate in CH_2Cl_2 as eluent to obtain the desired product **PTZ-OH** (compound **8**) as orange solid (120 mg, yield: 65%). 1H NMR (400 MHz, $CDCl_3$): *δ* 8.14 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.68 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.83 (m, 2H), 6.75 (brs, 1H), 3.81 (t, *J* = 5.3 Hz, 2H), 3.60 (t, *J* = 5.4 Hz, 2H), 3.42 (s, 3H), 3.38 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 161.95, 151.53, 149.83, 143.97, 131.47, 129.10, 127.80, 127.36, 126.04, 124.08, 123.68, 122.40, 117.54, 114.74, 114.02, 99.98, 61.98, 43.14, 35.71; HRMS (ESI): *m/z* calcd. 390.2024 $[M + K]^+$, found 390.1693 $[M + K].^+$

Synthesis of PTZ-P1:[4,6b] **PTZ-OH** (23 mg, 0.065 mmol) and L-Lactide (470 mg, 3.25 mmol) were taken along with dry and degassed toluene (1.0 mL) in a polymer glass vessel equipped with a septum. A solution of $Sn(Oct)_2$ (25 mg, 0.049 mmol) was added to the reaction vessel, and the solution was degassed for 30 minutes. The reaction vessel was immersed in a preheated oil bath at 115 °C for 15 h. The reaction was quenched by exposure to air. The solution was dissolved in CH_2Cl_2 and purified by precipitating from cold methanol to afford a yellowish-orange amorphous solid. The process was repeated several times to obtain a pure polymer, which was dried under vacuum at 40 °C for 48 h (345 mg). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.13 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.70 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.85-6.83 (m, 2H), 5.17-5.14 (q, *J* = 7.1 Hz, 100H), 4.37-4.35 (m, 1H), 3.74 (brs, 2H), 3.49 (brs, 2H), 3.43 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 300H). A conversion of 96% was noted in the ^{1}H NMR spectrum of the crude polymer. The number average molar weight (M_n) determined from size exclusion chromatography SEC analysis (PS standard, THF) was 8700 g/mol; Dispersity (*Đ*) = 1.65. The molecular weight estimated by end-group analysis from (i) ^{1}H NMR spectroscopy by comparing the integrals of the end-group (aromatic proton signals) and the integrals of the repeating chain unit of PLLA (**Figure S20**) = ~7,500 g/mol (DP = ~100); (ii) UV-Vis spectroscopy = ~9,000 g/mol.

Synthesis of PTZ-P2:[4,6b] **PTZ-OH** (5.01 mg, 0.014 mmol) and L-Lactide (103 mg, 0.713 mmol) were taken along with dry and degassed toluene (1.0 mL) in a glass vessel equipped with a septum. A solution of $Sn(Oct)_2$ (4.3 mg, 0.01 mmol) was added to the reaction vessel, and the solution was degassed for 30 minutes. The reaction vessel was immersed in a preheated oil bath at 115 °C for 15h. The reaction was quenched by exposure to air. The solution was dissolved with CH_2Cl_2 and purified by precipitating from cold methanol to afford a yellowish-orange amorphous solid. The process was repeated several times to obtain a pure polymer, which was dried under vacuum at 40 °C for 48 h (80 mg). 1H NMR (400 MHz, CDCl3): δ 8.13 (s, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.70 (s, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.85-6.83 (m, 2H), 3.49 (brs, 2H), 5.18-5.14 (q, *J* =

7.1 Hz, 235H), 4.38-4.33 (m, 1H), 3.43 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 705H). 95% conversion was noted from the ^{1}H NMR of the crude. The number average molar weight (M_n) determined from SEC analysis (PS standard, THF) was underestimated due to the lower hydrodynamic volume adopted by the higher DP **PTZ-P2** polymer, possibly due to its more compact structure formation in the eluent as compared to the standards used to calibrate the instrument. To avoid misinterpretation, we have not reported the molecular weight of **PTZ-P2** from the SEC analysis; Dispersity (*Đ*) =1.41. The molecular weight estimated by end-group analysis from (i) ^{1}H NMR spectroscopy by comparing the integrals of the end-group (aromatic proton signals) and the integrals of the repeating chain unit of PLLA (**Figure S21**) = ~17,400 g/mol (DP = ~235); (ii) UV-Vis spectroscopy = ~12,700 g/mol.

Synthesis of PY-P1:[4,6b] **PY-OH** (25 mg, 0.180 mmol) and L-lactide (478mg, 5.40 mmol) were taken along with dry and degassed toluene (1.0 mL) in a glass vessel equipped with a septum. A solution of $Sn(Oct)_2$ (33 mg, 0.75 mmol) was added to the reaction vessel, the solution was degassed for 30 minutes, and the reaction vessel was immersed in a preheated oil bath at 115 °C for 15 h. The reaction was quenched by exposure to air. The solution was dissolved with CH_2Cl_2 and purified by precipitating from cold methanol to afford a white solid. The process was repeated thrice to obtain a pure polymer, which was dried under vacuum at 40 °C for 48 h (600 mg). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.24 – 8.02 (m, 9H), 5.19-5.13 (q, *J* = 7.0 Hz, 93H), 4.36-4.34 (m, 1H), 1.58 (d, *J* = 7.1 Hz, 279H). 92% conversion was noted from the ^{1}H NMR spectrum of the crude polymer. The number average molar weight (M_n) calculated from SEC analysis (PS standard, THF) was 6600 g/mol; Dispersity (*Đ*) = 1.34. The molecular weight estimated by end-group analysis from (i) ^{1}H NMR spectroscopy by comparing the integrals of the end-group (aromatic proton signals) and the integrals of the repeating chain unit of PLLA (**Figure S22**) = ~6,900 g/mol (DP = ~93); (ii) UV-Vis spectroscopy = ~6000 g/mol.

Synthesis of **PY-P2** was earlier reported by us[4]

Synthesis of PY-P3: PY-OH (3.5 mg, 0.015 mmol) and L-lactide (599 mg, 4.153 mmol) were taken along with dry and degassed toluene (1.0 mL) in a glass vessel equipped with a septum. A solution of $Sn(Oct)_2$ (4.6 mg, 0.011 mmol) was added to the reaction vessel, and the solution was degassed for 30 minutes, and the reaction vessel was immersed in a preheated oil bath at 115 °C for 36 h. The reaction was quenched by exposure to air. The solution was dissolved with CH_2Cl_2 and purified by precipitating from cold methanol to afford a white solid. The process was repeated thrice to obtain a pure polymer, which was dried under vacuum at 40 °C for 48 h (500 mg). A conversion of 98% was noted from the ^{1}H NMR spectrum of the crude polymer. Due to the very high molecular weight of the **PY-P3** polymer, the proton signals for the end group (phenothiazine dye) could not be seen, making it impossible to estimate the molecular weight of the polymer by end-group analysis using the ^{1}H NMR technique. The

number average molar weight (M_n) from SEC analysis (PS standard, THF) was underestimated due to the lower hydrodynamic volume adopted by higher DP **PY-P3** polymer, possibly due to its more compact structure formation in the eluent as compared to the standards used to calibrate the instrument. To avoid misinterpretation, we have not reported the molecular weight of **PY-P3** from the SEC analysis; Dispersity (*Đ*) = 1.36. The molecular weight estimated by end-group analysis from UV-Vis spectroscopy = ~58,000 g/mol (DP = ~800).

Molecular weight determination by end-group analysis using UV-Vis Spectroscopy method:[5]

All the polymers contained a single chromophore (**PTZ**, **PY**) at the chain end. Thus, it was assumed that the concentration of the chromophore in the polymer chain is equal to the concentration of the polymer itself. i.e. [Chromophore] = [Polymer]. The absorption spectra of the known quantity of the polymers (in mg/mL) and their corresponding initiators (**PTZ-OH**/**PY-OH**) (in mM) were measured in THF at a concentration where they do not aggregate. Extinction coefficients were determined for the initiators from the Lambert-Beer Law equation. The chromophore concentration in each polymer chain was estimated in mM using the extinction coefficients of their respective initiators (assuming the extinction coefficients of the chromophore appended to the polymer chain and in the initiator are the same). The concentration obtained in mM was converted into g/mol to calculate the average molecular weights of the polymers.

Table S1: Molecular weight determination of different chromophore-appended PLLA polymers

Name	[a]DP (^{1}H NMR)	[b]M_n (^{1}H NMR) (g/mol)	[c]M_n (UV-Vis) (g/mol)	[d](*Đ*) (SEC)
PTZ-P1	~100	~7,500	~ 9,000	1.65
PTZ-P2	~ 235	~17,400	~12,700	1.41
PY-P1	~ 93	~ 6,900	~6,000	1.34
PY-P2	~ 245	~17,800	~14,000	1.43
PY-P3	~ 800*	-	~58,000	1.36

(a) Degree of polymerization (DP) determined by end-group analysis using ^{1}H NMR spectroscopy technique; (b) From the obtained DP, the number average molecular weight (M_n) was estimated using the formula M_n = DP X repeat unit mass + mass of the end-group; (*) The determination of DP and M_n for **PY-P3** was not possible by ^{1}H NMR spectroscopy method as the end-group signals were not visible in **PY-P3** due to its very high molecular weight. (c) M_n was determined by end-group analysis using the UV-Vis spectroscopy method. (d) Dispersity (*Đ*) was measured from size exclusion chromatography (SEC) using polystyrene standards and THF as eluent.

Experimental Procedures

Crystallization-driven self-assembly (CDSA) studies in iPrOH

Sample preparation techniques for PTZ-P1:

i) Uncontrolled (random) heating and cooling process (Method 1): Concentrated stock solutions of the polymers were prepared in $CHCl_3$. A measured quantity of the polymer solution was transferred into a glass vial. The $CHCl_3$ was removed by gently heating the solution to make a thin film in the vial. To this, 1.0 mL iPrOH was added dropwise so that the final concentration of the polymer becomes 0.1 mg/mL. The iPrOH solution was further heated vigorously for 1-2 minutes with a heat gun and then spontaneously cooled to room temperature to obtain the final solution. The solution was allowed to equilibrate at room temperature for 1.0 h before any physical studies were performed. The same sample preparation protocol was followed in each experiment unless specified separately. This sample preparation method produced diamond-shaped and truncated diamond-shaped 2D platelets of **PTZ-P1.** The same sample, heated to 60 ^{o}C for 4h and cooled rapidly to room temperature, produced hexagonal 2D platelets. No difference in morphology was observed if the sample vial was heated in a controlled manner instead of uncontrolled heating using a heat gun by placing it in a preheated oil bath set at 190 ^{o}C for 30 seconds, followed by cooling to room temperature and aging for 30 minutes (Figure S2c). At a lower temperature, incomplete dissolution of the **PTZ-P1** film in iPrOH led to an inhomogeneous solution, so we preferred using a heat gun for homogenous sample preparation.

For the co-assembly study of **PTZ-P1** with different donor polymers, the sample preparation technique is discussed under FRET studies.

ii) Isothermal crystallization at different annealing times (Method 2): Concentrated stock solutions of the polymers were prepared in $CHCl_3$. The measured quantity of the polymer solution was transferred into a glass vial. The $CHCl_3$ was removed by gently heating the solution to make a thin film in the vial. To this, 1.0 mL of iPrOH was added dropwise so that the final concentration of the polymer was 0.1 mg/mL. The iPrOH solution was further heated vigorously for 1-2 minutes with a heat gun and then immediately put into the preheated oil bath at 60 ^{o}C for 2 h, 3 h, and 4 h. Then the samples were cooled spontaneously to room temperature, and the morphology was checked after 18 h.

UV-Vis studies: UV-Vis absorption spectroscopy experiments were performed using a quartz cuvette of 10.0 mm path length at 25 °C. The solutions were prepared following the procedure described above.

Photoluminescence (PL) studies: The emission intensity of the polymer solutions in their self-assembled form in iPrOH was recorded in a quartz cuvette of 10 mm path length. The excitation wavelength (λ_{ex}) was maintained at 337 nm for **PY-P1**, **PY-P2**, and **PY-P3**. The excitation and emission bandwidths were kept at 1 nm, 1.5 nm, and 2 nm, respectively. For variable-temperature PL studies, the solutions of **PY-P1**, **PY-P2**, and **PY-P3** (0.1 mg/mL) in iPrOH were heated from 25 °C to 75 °C at an interval of 5 °C. Before taking the measurements, each time, the sample was allowed to stand for 2.0 minutes after the desired temperature was reached. The same procedure was followed for recording **PTZ-P1** (0.1 mg/mL) emission, and (λ_{ex}) was maintained at 430 nm. Excitation and emission bandwidths were kept at 2.5 nm each. For the co-assembly studies, the experimental conditions are mentioned in the respective figure captions.

Dynamic light scattering (DLS) studies: Experiments were carried out with a solution of **PTZ-P1** (0.1 mg/mL) in iPrOH. The solutions were prepared following the procedure described earlier. For high-temperature studies, the solution was heated from 25 ^{o}C to 75 ^{o}C, and the data was recorded at 75 ^{o}C. The same solution was cooled to 25 ^{o}C and allowed to stand for 5 minutes. Then, the data was recorded to check the reversibility of the crystallization-driven self-assembly (CDSA) process.

Confocal laser scanning microscopy (CLSM) studies: The solutions were prepared following the earlier procedure (**Methods 1** and **2**). For co-platelet fabrication, the sample preparation techniques are discussed under FRET studies. Measured aliquots of the different polymer solutions in iPrOH (Conc. = 0.05 mg/mL) were drop-cast on microscope glass slides and slowly air-dried for 24 h before imaging.

Atomic force microscopy (AFM) studies: The solutions of **PTZ-P1** in iPrOH were prepared following the procedures (**Methods 1** and **2**) described earlier. A measured aliquot of the polymer solution (**PTZ-P1**; Conc. 0.05 mg/mL) was drop-cast on a mica surface and slowly air-dried for 24 hours before imaging. **Method 1** produced diamond-shaped platelets, and **Method 2** generated hexagonal platelets, which were analyzed by AFM studies.

Transmission electron microscopy (TEM) studies: The solutions were prepared following the procedures (**Methods 1** and **2**) described earlier. A measured aliquot of the polymer solution (**PTZ-P1**; Conc. 0.05 mg/mL) in iPrOH was drop-cast on a carbon-coated copper grid and slowly air-dried for 24 hours prior to imaging. **Method 1** produced diamond-shaped platelets, and **Method 2** generated hexagonal platelets, which were analyzed by TEM studies. Low-dose SAED was performed on a Jeol 2100 LaB6 transmission electron microscope operating at 200 kV.

Differential scanning calorimetry (DSC) and Wide-angle X-ray diffraction (WAXD): A solution of **PTZ-P1** was first prepared in iPrOH using the previously mentioned technique (**Method 1**) and drop-cast on a glass slide to make a thin film of appropriate thickness. To obtain the material in powder form, the thin film was scraped off the glass slide. The resultant crystalline power was used for WAXD and DSC analysis.

Förster Resonance Energy Transfer (FRET) studies:

Sample preparation for (1:1) Donor : Acceptor co-assembly: Concentrated stock solutions of the donor (**PY-P1**, **PY-P2,** and **PY-P3**) and the acceptor (**PTZ-P1**) were prepared separately in $CHCl_3$. Measured aliquots of the stock solutions of **PY-P1** and **PTZ-P1** (**CoAs-1**), **PY-P2** and **PTZ-P1** (**CoAs-2**), and **PY-P3** and **PTZ-P1** (**CoAs-3**) were taken together in three different vials. The organic solvent was evaporated by heating to make a thin film. This was followed by the dropwise addition of 1.0 mL of iPrOH so that the individual polymer concentration became 0.1 mg/mL in the co-assembly. The resultant solution was randomly heated for about 1-2 minutes with a heat gun and kept for spontaneous cooling at room temperature. Finally, the solution was equilibrated for 1 hour. To monitor the evolution of the FRET process, the emission spectra of the three different co-assembled solutions (**CoAs-1**, **CoAs-2**, and **CoAs-3**) were recorded at the donor (**PY-P1**, **PY-P2**, **PY-P3**) excitation. The acceptor (**PTZ-P1**) emission spectra were compared in the presence and absence of the donor.

Dilution experiment with $CHCl_3$ and temperature-dependent studies: A similar procedure was followed for the sample preparation mentioned above for **CoAs-1**, **CoAs-2**, and **CoAs-3**. The individual polymer **PY-P1**, **PY-P2**, **PY-P3,** and **PTZ-P1** concentrations in the co-assembled solutions were maintained at 0.1 mg/mL each. To this solution, a measured volume of $CHCl_3$ was added stepwise, and the emission spectra were recorded at the donor (**PY-P1**, **PY-P2,** and **PY-P3**) excitation to monitor the disappearance of the FRET. For variable-temperature FRET studies, the solutions of **PY-P1**, **PY-P2**, and **PY-P3** (0.1 mg/mL) in iPrOH were heated from 25 °C to 75 °C at an interval of 5 °C. Before taking the measurements, each time, the sample was allowed to stand for 2.0 minutes after the desired temperature was reached.

Time-correlated single photon counting (TCSPC) measurements:[4,6] The intensity average lifetimes (τ_{avg}) of **PY-P1**, **PY-P2,** and **PY-P3** in iPrOH in their self-assembled state and co-assembled state in the presence of **PTZ-P1** were compared. Individual concentrations of **PY-P1**, **PY-P2**, **PY-P3,** and **PTZ-P1** were maintained at 0.1 mg/mL in the co-assembly. The lifetimes were calculated using the following equation.

$$\tau_{avg} = \sum a_i \tau_i^2 / \sum a_i \tau_i$$

where "a" represents the decay contribution corresponding to each lifetime (τ).

Table S2: Estimating the intensity average lifetimes (τ_{avg}) of donor polymers (**PY-P1**, **PY-P1**, and **PY-P1**) in their self-assembled states in iPrOH and co-assembled states in the presence of the acceptor polymer **PTZ-P1** (λ_{ex} = 280 nm, λ_{em} = 374 nm)

sample	τ_1	τ_2	τ_3	a_1	a_2	a_3	X^2	τ_{avg} (ns)
PY-P1	33.29	115.38	-	19.82	80.18	-	1.15	109.91
CoAs-1	6.25	16.85	-	41.41	58.59	-	0.94	14.64
PY-P2	26.07	95.88	8.34	38.78	32.06	29.16	1.09	74.65
CoAs-2	5.08	29.83	-	71.11	28.89	-	1.07	22.52
PY-P3	24.81	7.74	98.41	45.57	26.03	28.40	1.08	73.10
CoAs-3	3.70	15.60	63.31	43.93	46.82	9.25	0.96	33.00

Table S3: Estimating the intensity average lifetimes (τ_{avg}) of the pyrene excimer emission using the above-mentioned equation for **PY-P1**, **PY-P2**, and **PY-P3** in iPrOH in their self-assembled states (λ_{ex} = 280 nm, λ_{em} = 472 nm)

sample	τ_1	τ_2	τ_3	a_1	a_2	a_3	X^2	τ_{avg} (ns)
PY-P1	65.22	146.87	-	74.74	25.26	-	1.03	100.0
PY-P2	7.48	32.09	2.47	19.27	28.32	52.41	1.04	25.85
PY-P3	11.24	19.47	2.49	11.39	4.08	84.53	1.05	8.40

FRET distance (r) determination: The detailed method is reported by us elsewhere.[6b] The following equation 2 was used to compute the Förster distance (r) between the donor (**PY-P1**, **PY-P2**, and **PY-P3**) and the acceptor (**PTZ-P1**) polymers.

$$r^6 = [R_0^6(1 - E)]/E \qquad (2)$$

The energy efficiency was calculated using the intensity average lifetimes of the donors in the presence and absence of the acceptor (τ_{DA} and τ_D, respectively) by using equation 3 provided below

$$E = 1 - (\frac{\tau_D}{\tau_D}) \quad (3)$$

R_0 represents the distance between the donor and acceptor dye at a 50 % energy transfer efficiency, which was determined following the previously reported procedure.[6b]

Average Area Determination:[7] 2D platelet area distributions were determined using the software program Image J. For the statistical analysis, several discrete 2D platelet images were traced by the software to get information about their area. The number average area (A_n) and weight average area (A_w) were calculated using the following equation (*N*: number; *A*: area of the 2D platelets).

$$A_n = \frac{\sum_{i=1}^{n} N_i A_i}{\sum_{i=1}^{n} N_i} \; ; \; A_w = \frac{\sum_{i=1}^{n} N_i A^2{}_i}{\sum_{i=1}^{n} N_i A_i}$$

Additional Figures

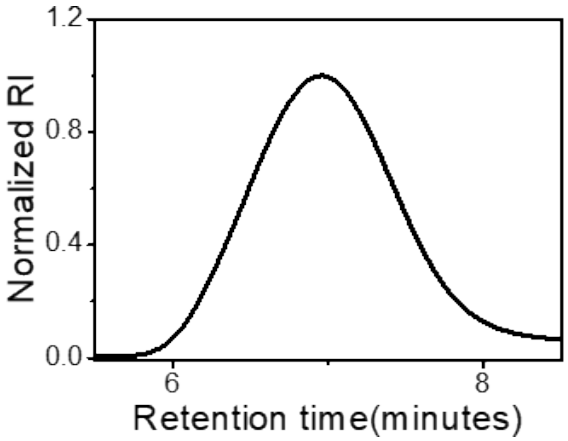


Figure S1. Size exclusion chromatograms of **PTZ-P1** in THF.

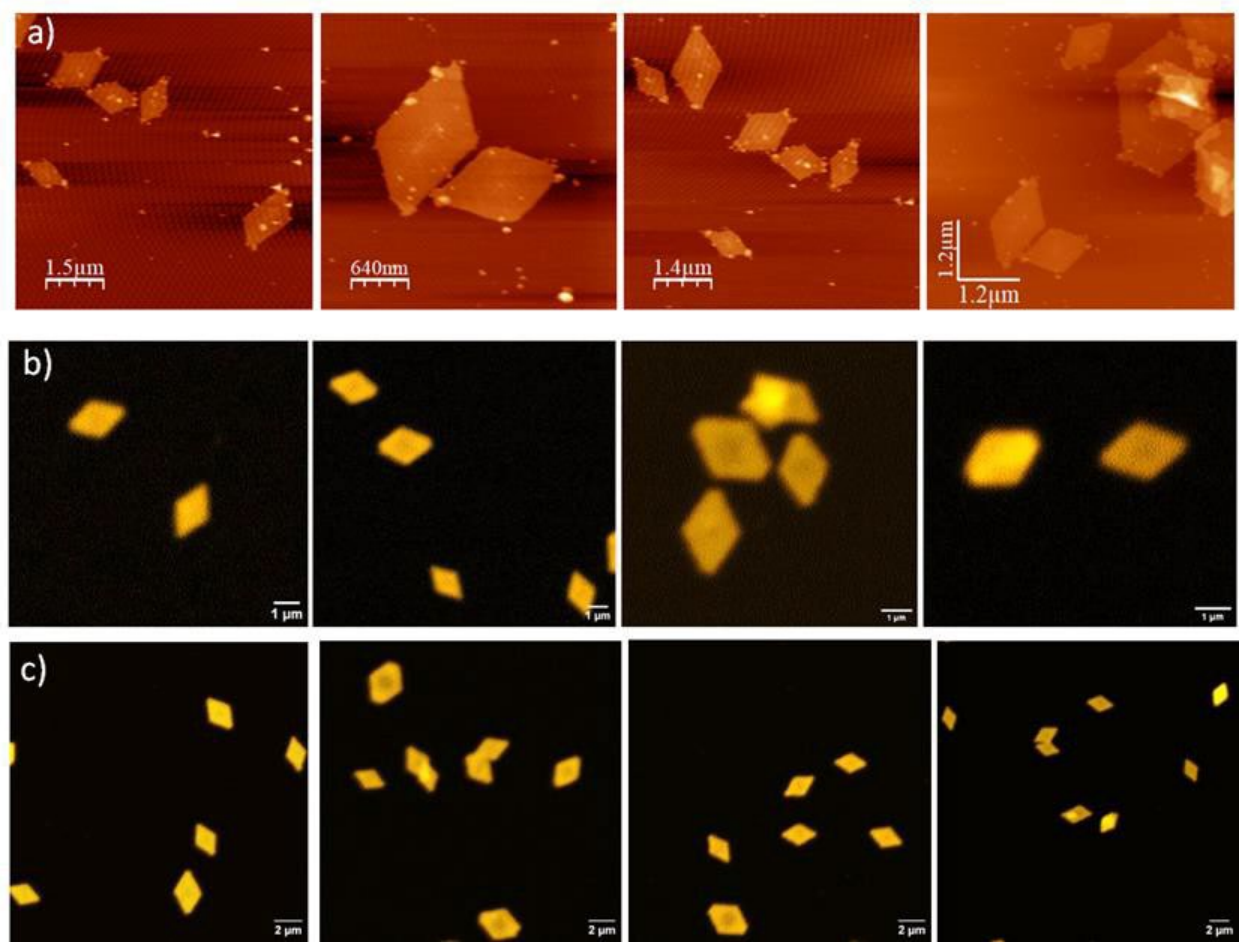


Figure S2. a) AFM images and b) CLSM images captured from self-assembled **PTZ-P1** in iPrOH at Conc. = 0.05 mg/mL (sample prepared by uncontrolled heating and cooling following **Method 1**); c) CLSM images from a self-assembled **PTZ-P1** in iPrOH heated at 190 ^{o}C for 30 seconds and then cooled to room temperature. Apparently, no difference in morphology was observed between controlled and uncontrolled heating.

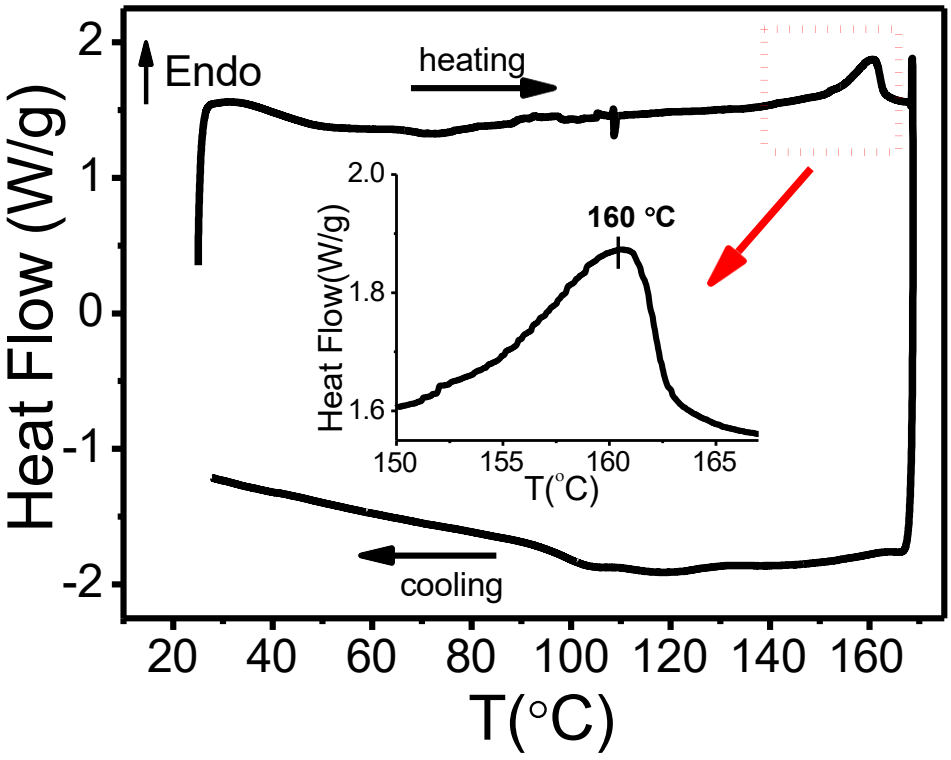


Figure S3. Differential scanning calorimetry (DSC) plot of **PTZ-P1** (inset showing a zoomed image of the melting curve). A powdered sample of **PTZ-P1** for analysis was obtained by slowly drying its self-assembled solution in iPrOH.

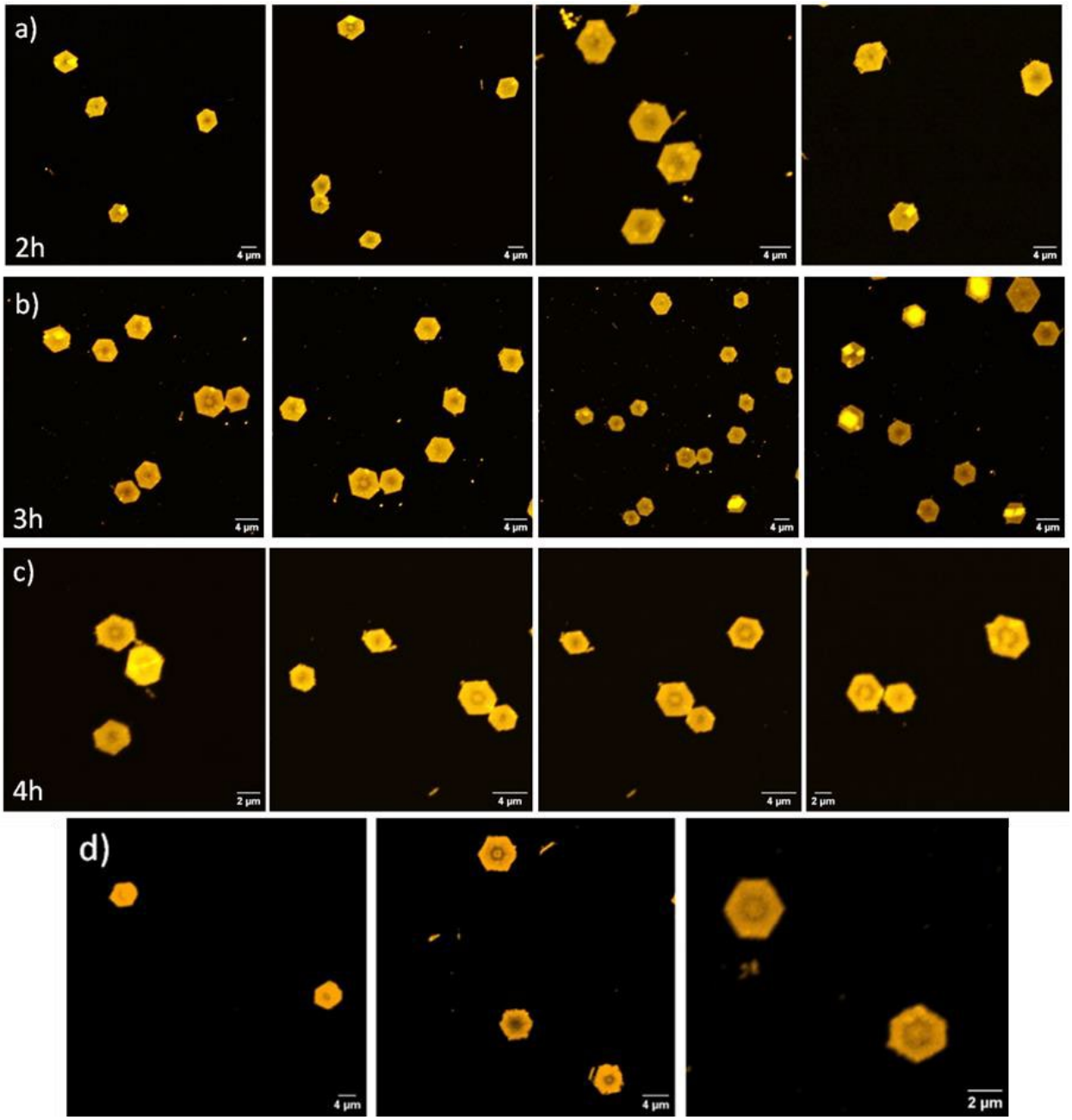


Figure S4. CLSM images of self-assembled **PTZ-P1** in iPrOH obtained following **Method 2** by sample annealing at 60 °C for a) 2h, b) 3h, and c) 4h; d) annealing of the preformed diamond-shaped platelets (generated by **Method 1**) for 4h at 60 °C. Conc. = 0.05 mg/mL.

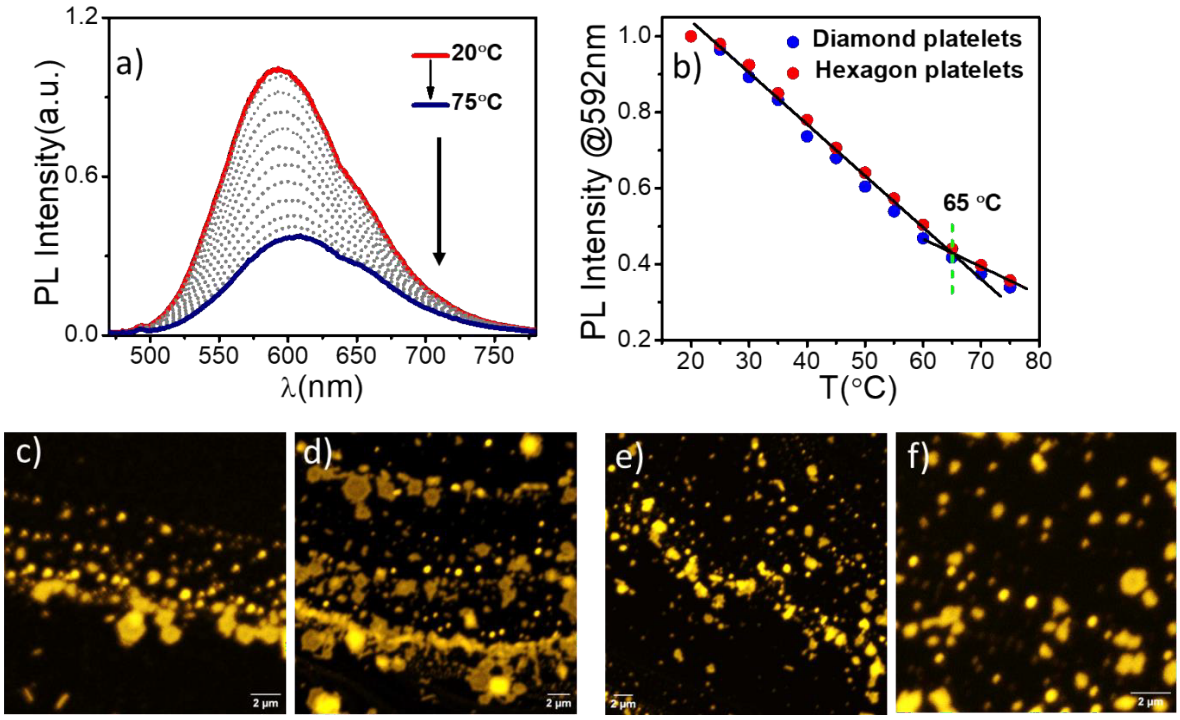


Figure S5. a) Variable-Temperature (VT) PL studies of **PTZ-P1** in iPrOH. Sample prepared by heating at 60 °C for 4h (λ_{ex}= 430 nm); excitation and emission slit = 2.5 nm/2.5 nm; b) Comparison of the disassembly temperature of the self-assembled diamond- and hexagonal platelets from PL-Intensity vs. temperature plots in iPrOH (λ_{em} = 592 nm); c) CLSM images obtained from **PTZ-P1** in iPrOH when heated at c-d) 65 °C and e-f) 70 °C.

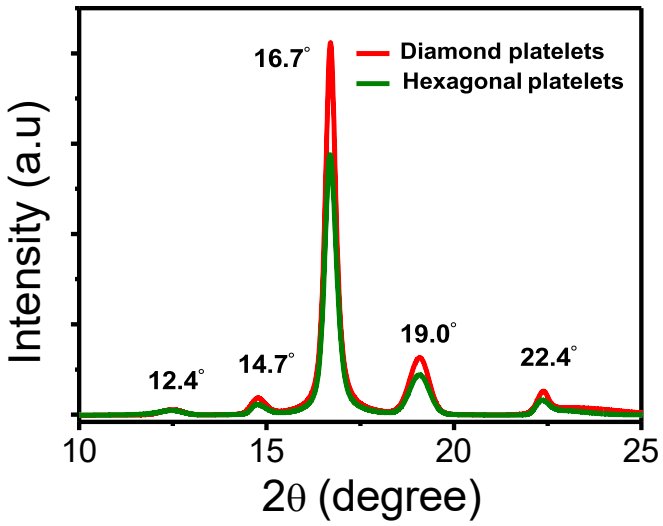


Figure S6. Comparison of WAXRD patterns of **PTZ-P1** powder obtained by slowly drying its self-assembled solution in iPrOH prepared by **Method 1** (uncontrolled heating and cooling) and **Method 2** (annealing at 60 °C for 4 h followed by spontaneous cooling).

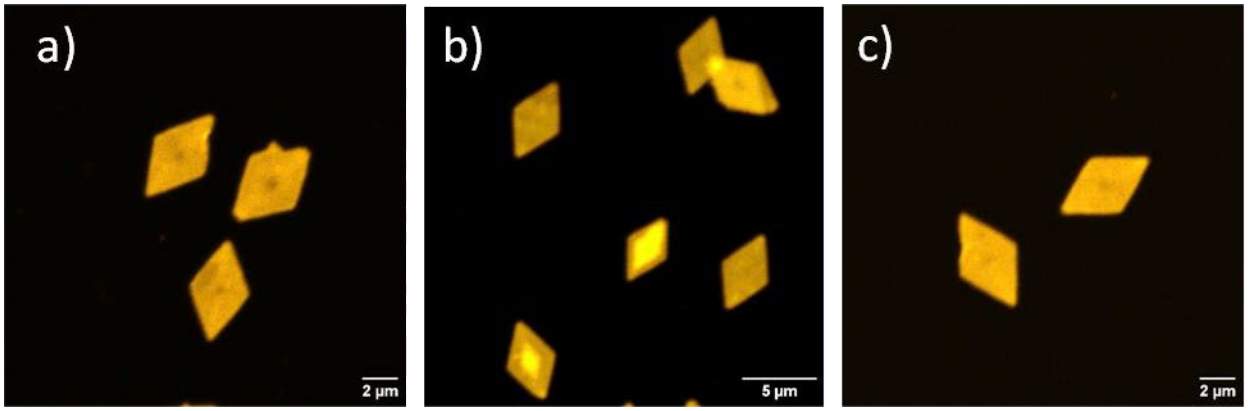


Figure S7. CLSM images (a-c) of self-assembled **PTZ-P2** in iPrOH showing diamond-shaped platelets obtained by **Method 1** (sample prepared by uncontrolled heating and cooling). Conc. = 0.05 mg/mL.

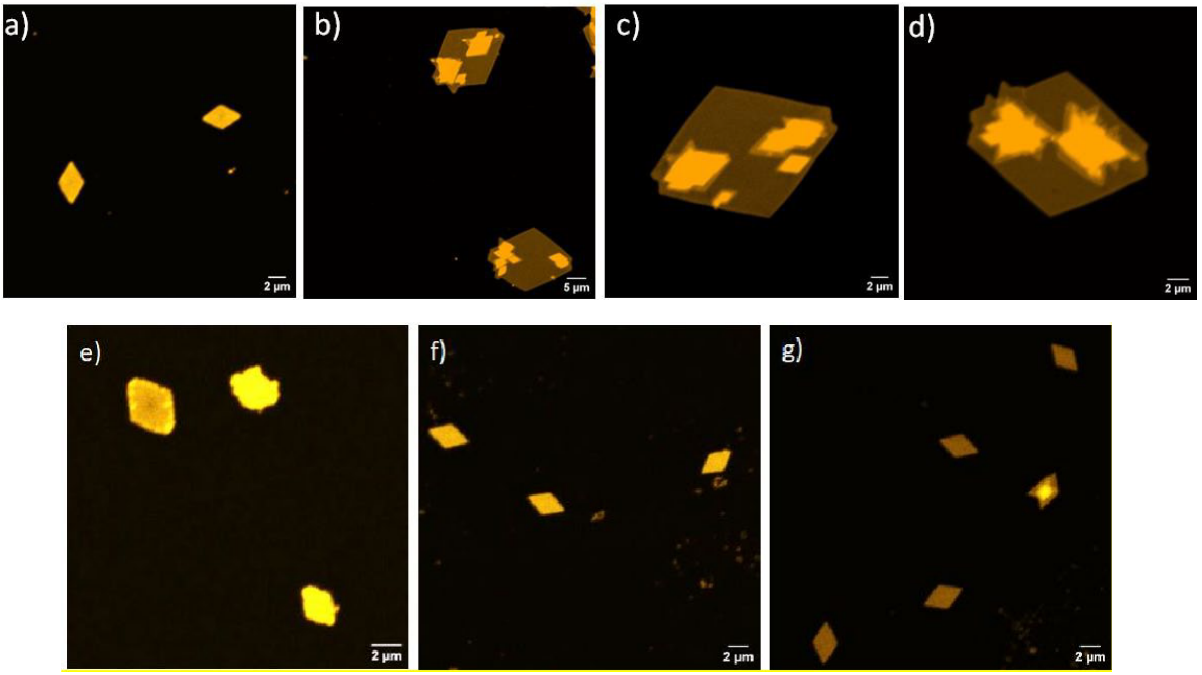


Figure S8. CLSM images of self-assembled **PTZ-P2** obtained by **Method 2** showing a) diamond-shaped platelets when the sample was annealed at 60 °C for 4h followed by spontaneous cooling and (b-d) enlarged and truncated diamond-shaped platelets when the sample was annealed at 80 °C for 4h followed by spontaneous cooling. (e-g) CLSM images showing reduction in the platelet size when the same sample was annealed at 80 °C for 20h followed by spontaneous cooling. Conc.= 0.05 mg/mL in iPrOH.

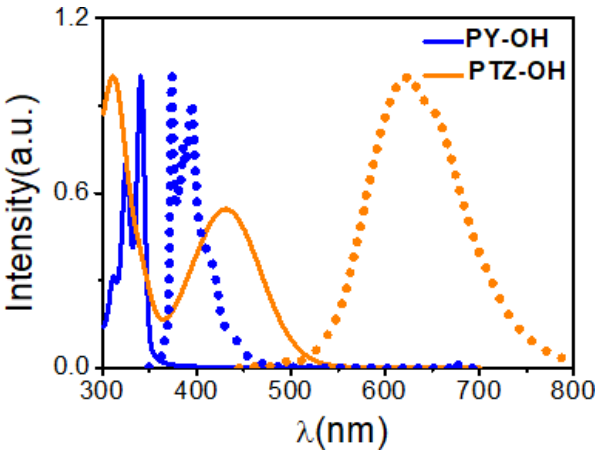


Figure S9. a) Normalized absorbance spectra (solid curves) and emission spectra (dashed curves) of **PY-OH** (blue trace, λ_{ex}= 337 nm) and **PTZ-OH** (orange trace, λ_{ex}= 430 nm) in iPrOH.

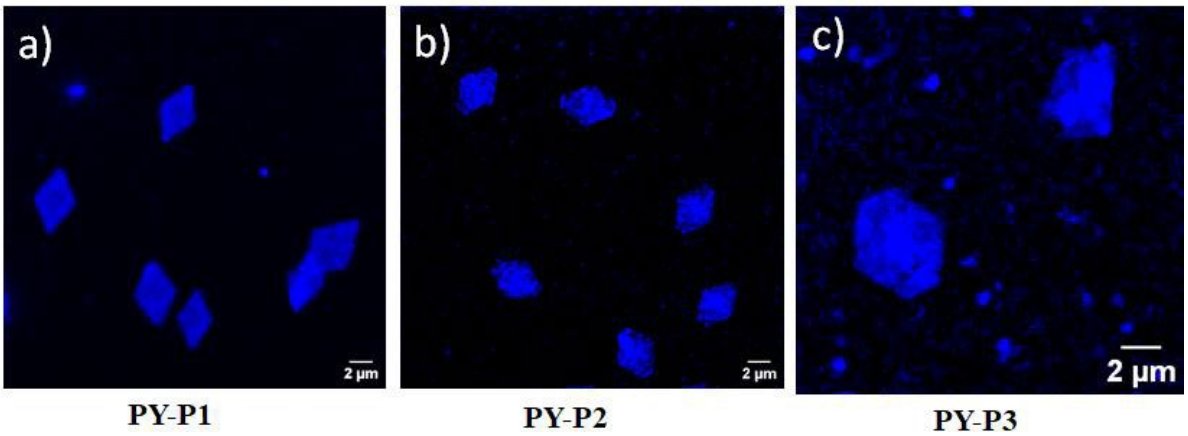


Figure S10. CLSM images of self-assembled a) **PY-P1**, b) **PY-P2**, and c) **PY-P3** in iPrOH. Conc. = 0.05 mg/mL.

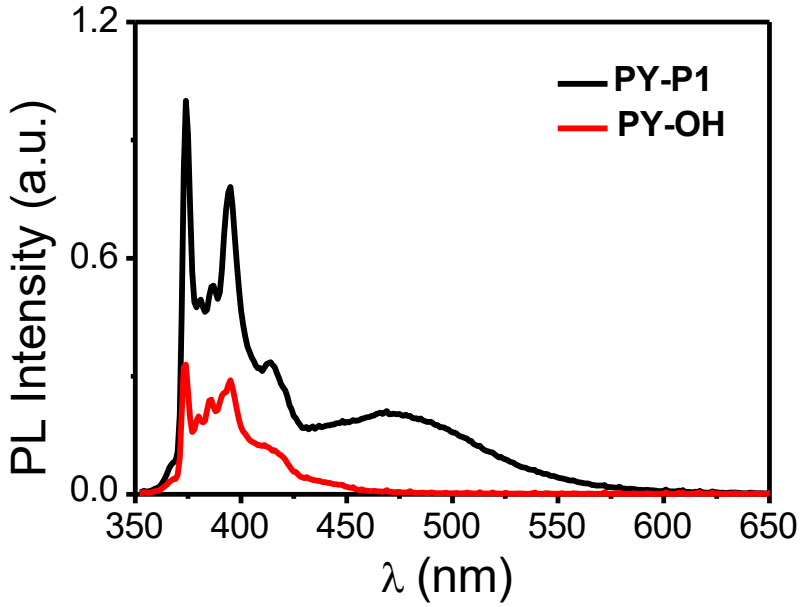


Figure S11. Absorption normalized PL spectra of **PY-P1** (Conc. = 0.1 mg/mL) and **PY-OH** (Conc. = 4 µm) in iPrOH; path length = 10 mm, excitation and emission slit = 1 nm/1 nm, λ_{ex} = 337 nm. At the same dye concentration, **PY-OH** does not show excimer band formation.

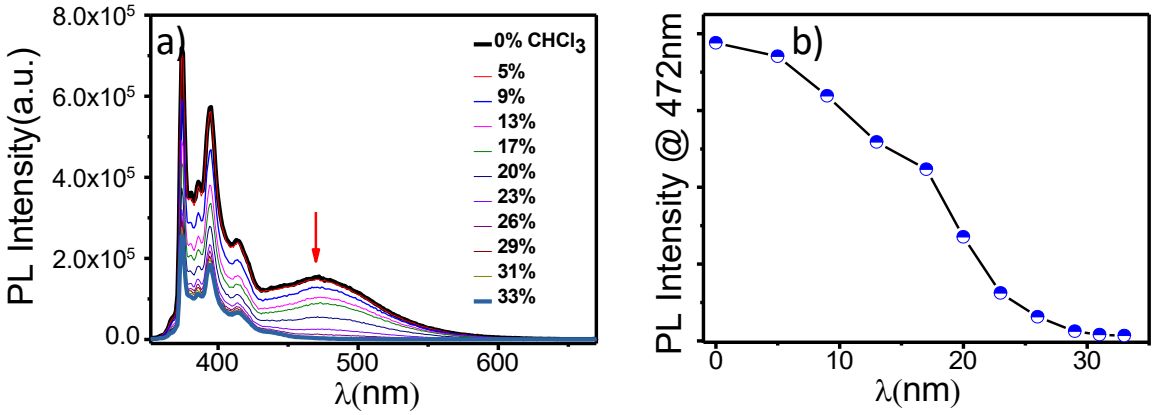


Figure S12. a) Change in the PL spectra of self-assembled **PY-P1** in iPrOH as a function of $CHCl_3$ addition; b) Pyrene excimer band intensity vs. $CHCl_3$ addition plot. λ_{ex}= 337 nm, slit = 1 nm/1 nm.

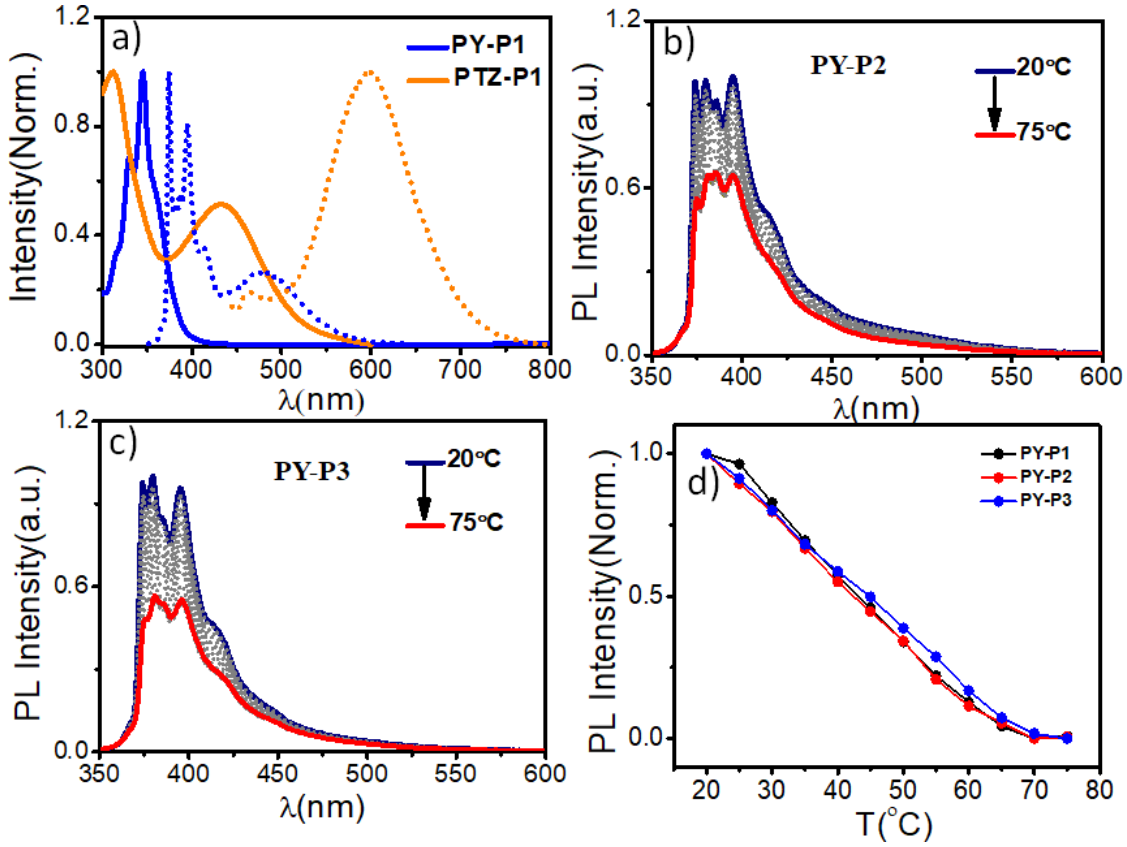


Figure S13. a) Normalized absorbance spectra (solid curves) and emission spectra (dashed curves) of **PY-P1** (blue trace, λ_{ex}= 337 nm) and **PTZ-P1** (orange trace, λ_{ex}= 430 nm) in iPrOH; VT-PL spectra of self-assembled **PY-P2** (b) and **PY-P3** (c) in iPrOH; (d) Comparison of disassembly temperature of **PY-P1**, **PY-P2** and **PY-P3** from PL-Intensity vs. temperature plot (λ_{em} = 374 nm); Conc. = 0.1 mg/mL; Solvent = iPrOH, λ_{ex} = 337 nm.

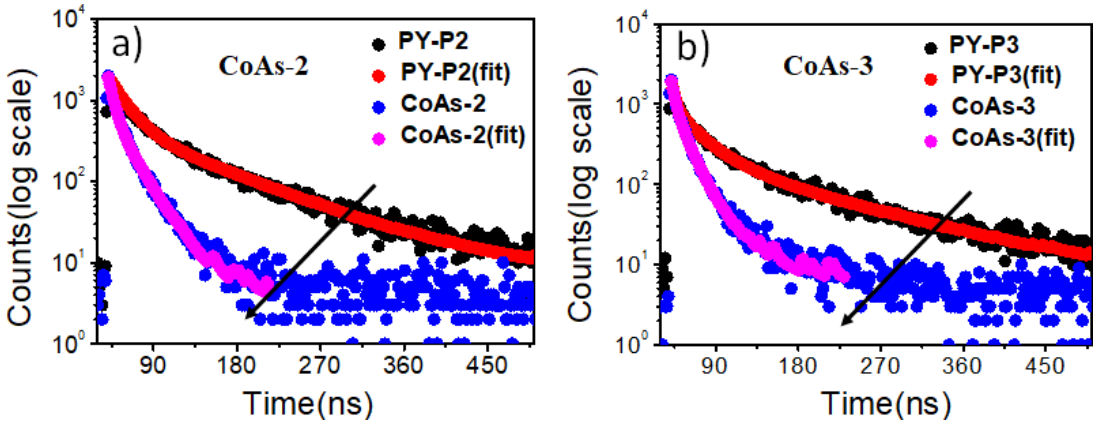


Figure S14. Compared time-resolved fluorescence decay profiles of a) **PY-P2** and **CoAs-2** (1:1 **PY-P2**+**PTZ-P1**), and b) **PY-P3** and **CoAs-3** (1:1 **PY-P3**+**PTZ-P1**) in iPrOH (λ_{ex} = 280 nm; λ_{em} = 374 nm).

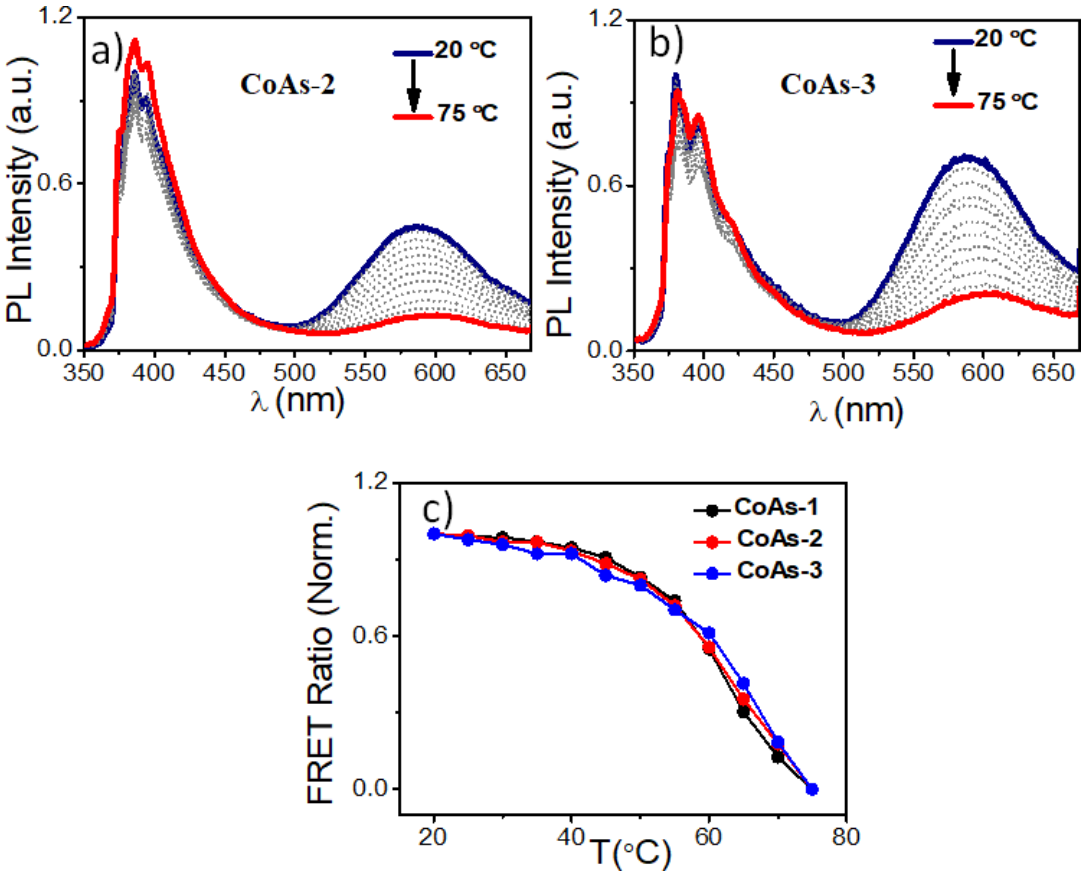


Figure S15. Variable-Temperature (VT) PL studies of 1:1 co-assembly of a) **PY-P2** + **PTZ-P1** (**CoAs-2**), and b) **PY-P3** + **PTZ-P1** (**CoAs-3**) from 20 °C to 75 °C at 5 ° interval (λ_{ex} = 337 nm, slit = 1.5 nm/1.5 nm); c) Stack plot of FRET ratio of **CoAs-1**, **CoAs-2** and **CoAs-3** as function of temperature changes to compare their disassembly temperatures; solvent = iPrOH. λ_{ex} = 337 nm.

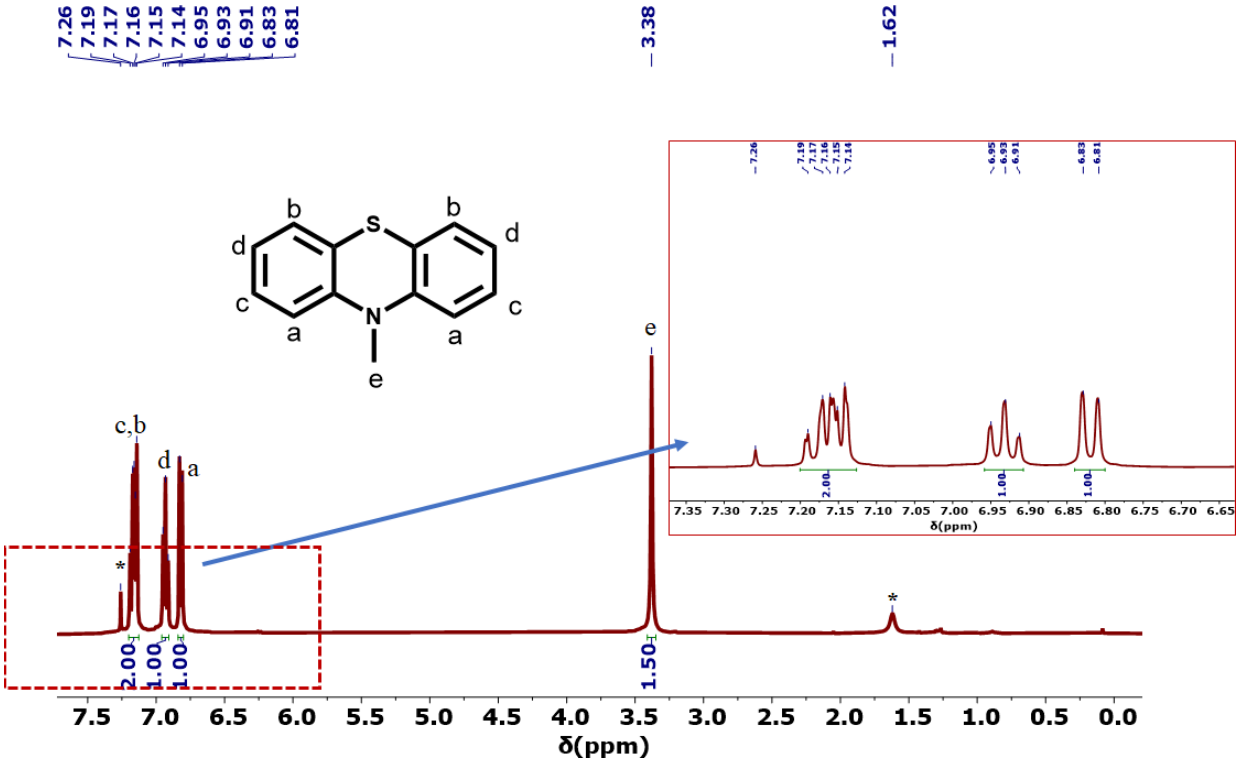


Figure S16. ^{1}H NMR spectrum of compound **3** in $CDCl_3$. (*) indicates residual solvent peaks.

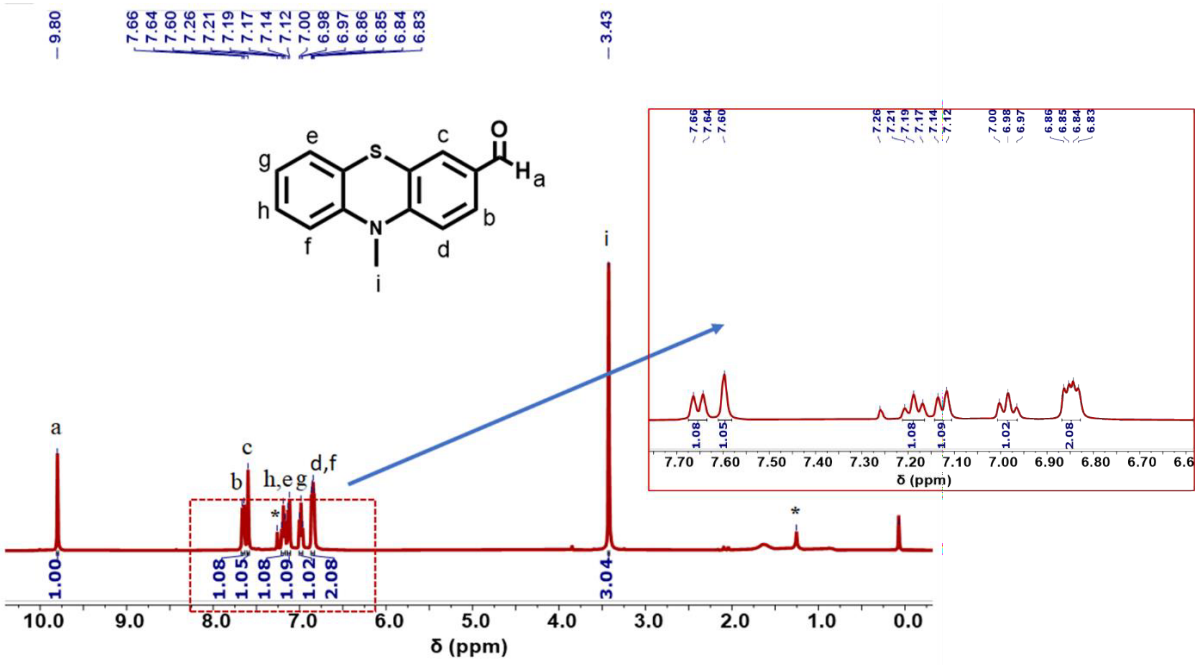


Figure S17. ^{1}H NMR spectrum of compound **4** in $CDCl_3$. (*) indicates residual solvent peaks.

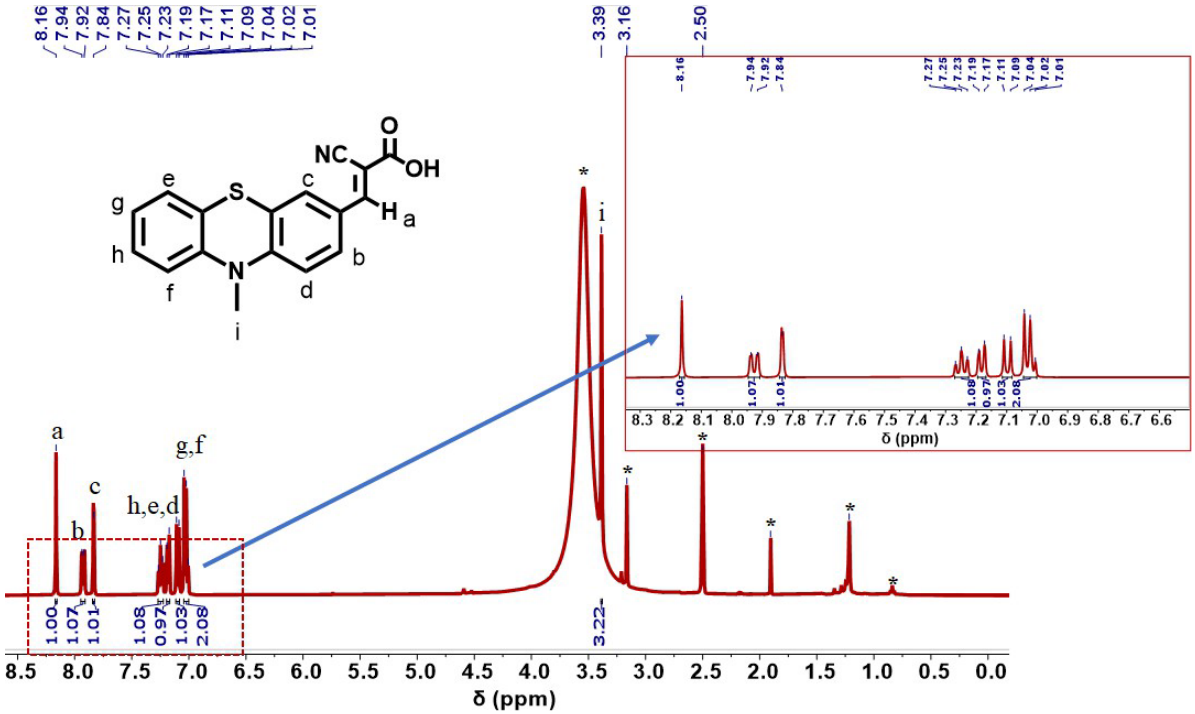


Figure S18: ^{1}H NMR spectrum of compound **6** in DMSO-d_6. (*) indicates residual solvent peaks.

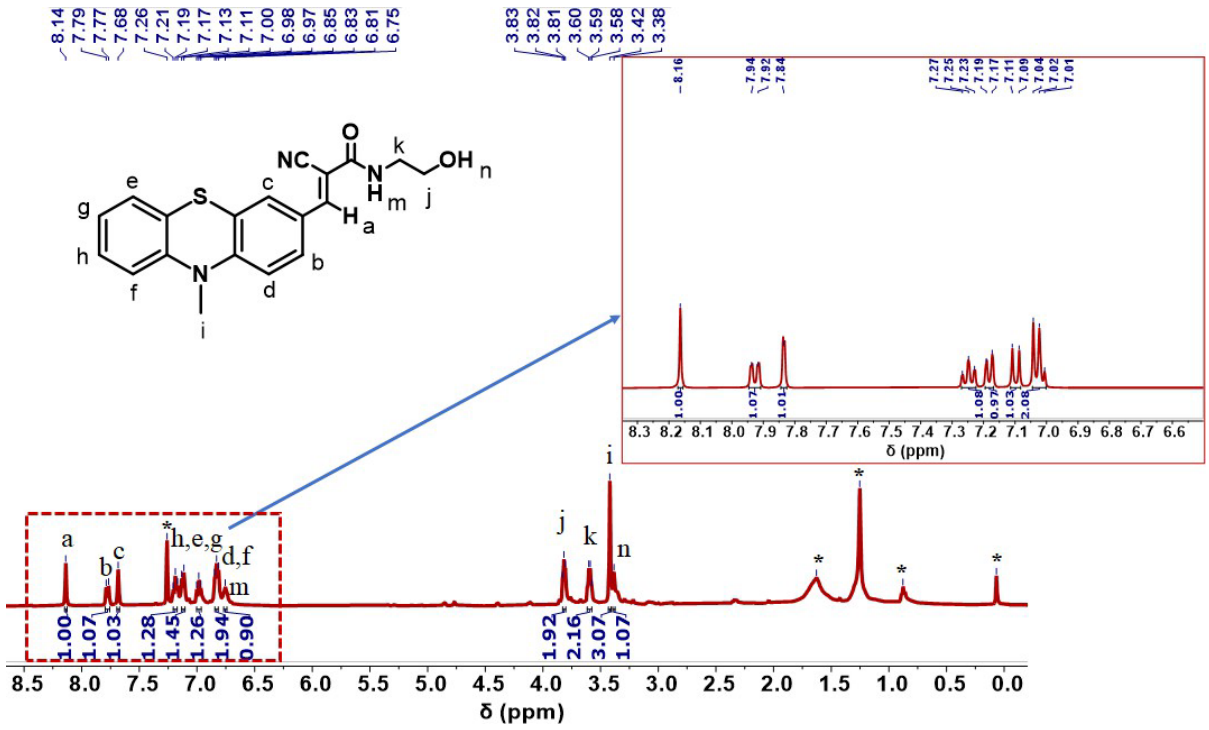


Figure S19: ^{1}H NMR spectrum of compound **8** in $CDCl_3$. (*) indicates residual solvent peaks.

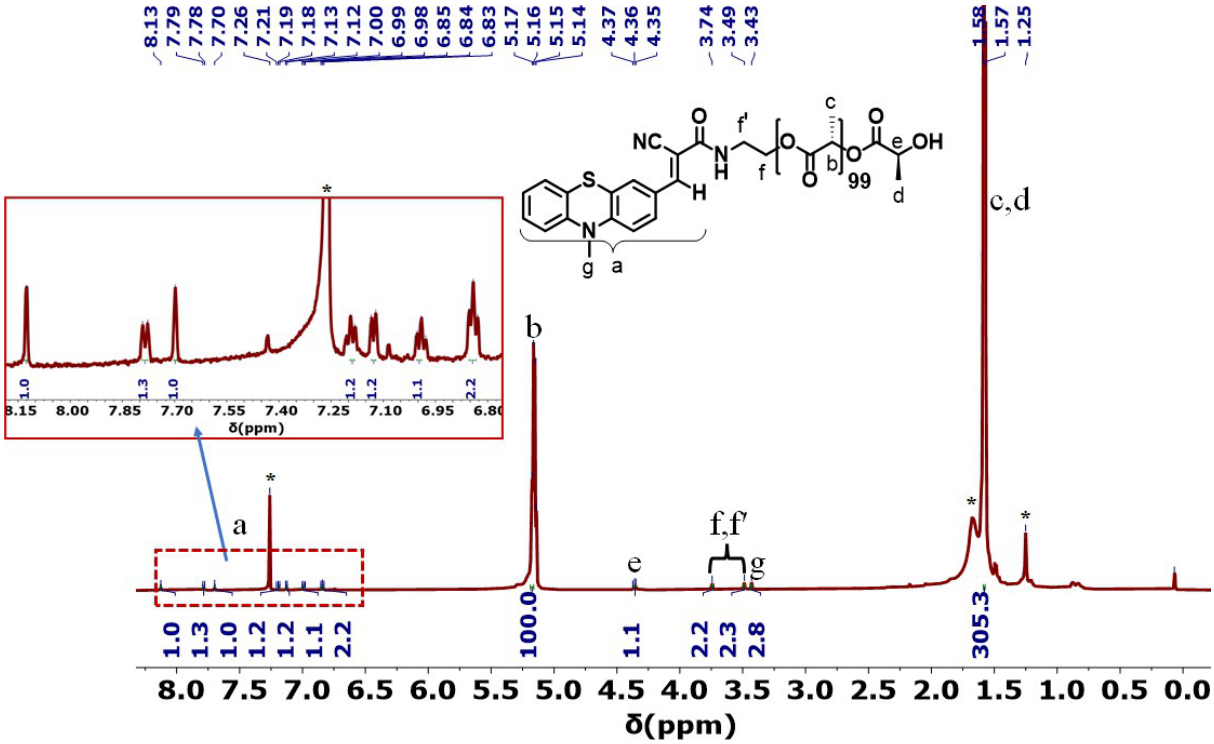


Figure S20. ^{1}H NMR spectrum of **PTZ-P1** in $CDCl_3$. (*) indicates residual solvent peaks.

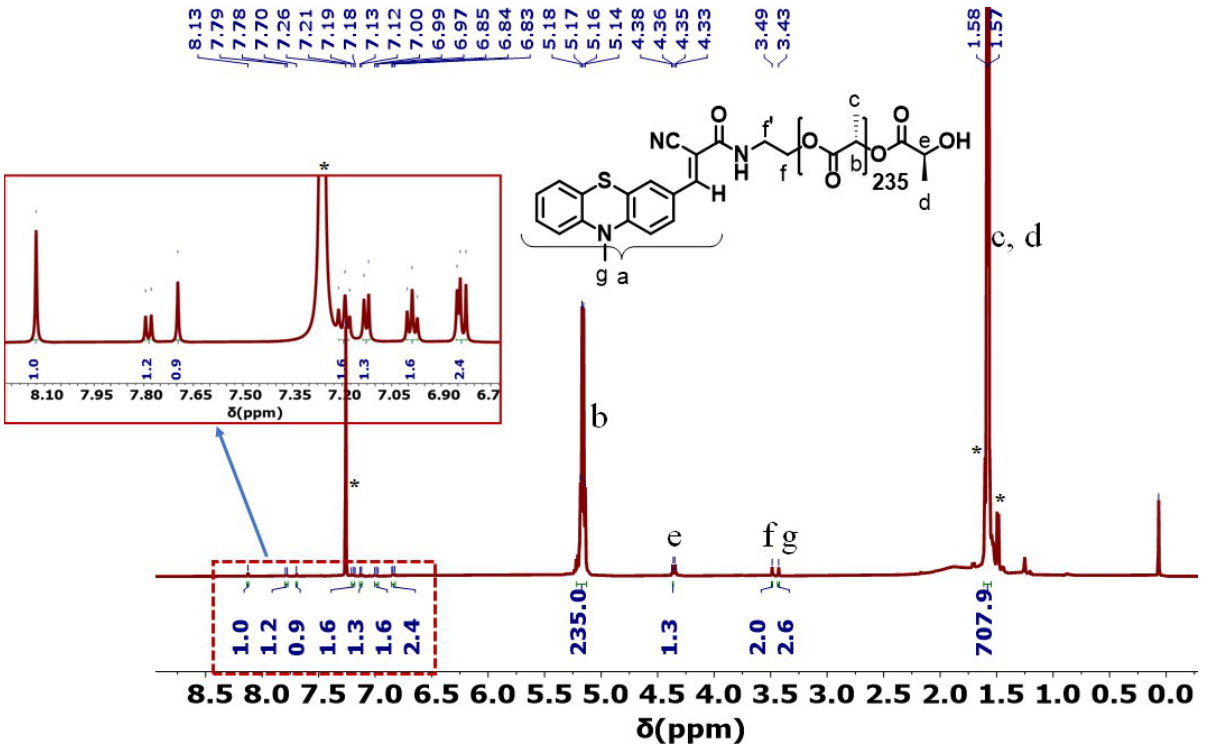


Figure S21. ^{1}H NMR spectrum of **PTZ-P2** in $CDCl_3$. (*) indicates residual solvent peaks.

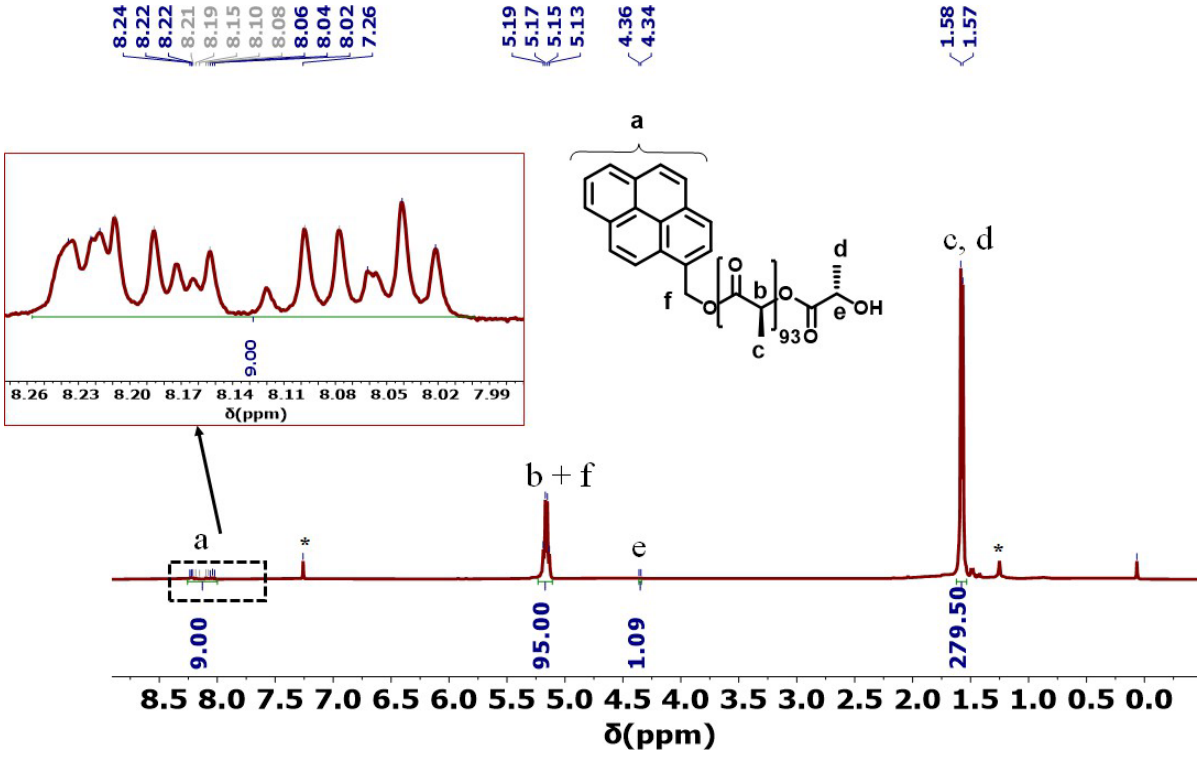


Figure S22. ^{1}H NMR spectrum of **PY-P1** in $CDCl_3$. (*) indicates residual solvent peaks.

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