Supporting Information

Exciplex emissive supramolecular polymer formed by tuning molecular conformation

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1. General

The ¹H and ¹³C NMR spectra were taken on a Bruker DRX 300. The highresolution mass spectra (HR MS) were measured by electrospray ionization (ESI) with a microTOF Focus spectrometer from SYNAPT G2 (Waters, U.K.). X-ray diffraction (XRD) pattern was recorded on a Rigaku model Miniflex600 X-ray diffractometer with a Cu Kα radiation source. A UV-visible spectrophotometer (Thermo Evolution 600) was used to obtain the absorption spectra. IR spectra were obtained for KBr pellets, in the range 400–4000 cm⁻¹, with a Shimadzu FTIR 8400S instrument.

1.1 AFM Observations

Atomic force microscope (AFM) imaging was performed by using XE-100 and a PPP-NCHR 10 M cantilever (Park systems). The AFM samples were prepared by spin-coating (1500 rpm) onto freshly cleaved Muscovite Mica, and images were recorded with the AFM operating in noncontact mode in air at RT with resolution of 1024×1024 pixels, using moderate scan rates (0.3 Hz).

1.2 Circular Dichroism Studies

The CD spectra were recorded on a Jasco J-815 CD spectrophotometer. CD spectra were determined over the range of 190-600 nm using a quartz cell with 2 mm path length. Scans were taken at a rate of 100 nm/min with a sampling interval of 1.0 nm and response time of 1s. The scans were acquired for the solution sample directly at room temperature.

1.3 Thermodynamic Studies

The molar fraction of aggregated molecules (α_{agg}) at a certain temperature was calculated from the absorption intensity at 360 nm based on Eq. 1, in which Abs(agg) and Abs(mono) are the absorption intensities of fully aggregated (at the lowest temperature) and purely monomeric states (at the highest temperature), respectively, and Abs(T) is the absorption intensity at a given temperature (T).

$$\alpha_{agg} = 1 - \frac{Abs(agg) - Abs(T)}{Abs(agg) - Abs(mono)}$$
(1)

The plot of α_{agg} versus temperature provides heating curves with nonsigmoidal (cooperative

mechanism) shape, which were fitted using the models proposed by Meijer et al. (for cooperative mechanism). The standard values of enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were calculated using the van't Hoff equation.

The van't Hoff plots were produced using equation by a method that has been proposed in previous literature. The values for the entropy change (ΔS) and enthalpy change (ΔH) as used in the cooperative supramolecular polymerization models were obtained by fitting to the heating or cooling curves. These heating or cooling curves where obtained by temperature dependent circular dichroism (CD) and UV-vis spectra.

2. Synthesis and characterization

Unless otherwise noted, chemical reagents and solvents were purchased from commercial suppliers (Tokyo Chemical Industry (TCI), Sigma Aldrich) and used without further purification.



2.1 Synthesis of Bipy-1-b

To a mixture of the 2,2'-bipyridine-5,5'-dicarboxylic acid (**Bipy-1-c**) (1.0 g, 4.1 mmol), *D*-alanine methyl ester hydrochloride (1.20 g, 8.6 mmol), HOBt·H₂O (1.11 g, 8.2 mmol) and EDC·HCl (2.36 g, 12.3 mmol) in CH₂Cl₂/DMF (4:1, 25 mL) was added TEA 3.4 mL at 0 °C. The reaction mixture was stirred for 1 h and was heated up to room temperature. After stirring for 2 days at room temperature, the mixture was extracted with CH₂Cl₂ (3 x 30 mL). The combined organics were washed with brine, dried (Na₂SO₄), and concentrated. The resulting crude product was purified by recrystallization from CH₂Cl₂/ether to give a white solid, compound **Bipy-1-b** (1.02 g, 60%). Decomposition 260 °C; IR (KBr pellet): 3320, 3048, 2997, 2953, 1735, 1635, 1591, 1527, 1460, 1320, 1279, 1241, 1216, 1169 cm⁻¹; ¹H NMR (300 MHz,

DMSO- d_6) δ = 9.27 – 9.02 (m, 4H), 8.63 – 8.52 (m, 2H), 8.43 (dd, J = 8.3, 2.2 Hz, 2H), 4.55 (p, J = 7.3 Hz, 2H), 3.68 (s, 6H), 1.45 (d, J = 7.3 Hz, 6H); ¹³C NMR (75 MHz, DMSO- d_6) δ = 173.41, 164.99, 156.98, 149.16, 137.04, 130.01, 121.08, 52.47, 48.83, 17.18; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): m/z calculated for C₂₀H₂₂N₄O₆ [M+H]⁺: 415.1618, found: 415.1618.

2.2 Synthesis of Bipy-1-a

A solution of **Bipy-1-b** (0.5 g, 1.2 mmol) in a mixture with EtOH (40 mL) was heated to reflux. The reaction mixture was then added to aqueous 1 M NaOH. After refluxing for 12 h, the organic solvents were removed in vacuo, and water (15 mL) was added. The remaining aqueous solution was acidified to pH 3 by adding 3 N HCl. The resulting precipitate was filtered and washed with water. The precipitate was dried under vacuum to give **Bipy-1-a** as a white solid in 75% yield. Decomposition 298 °C; IR (KBr pellet): 3567, 3321, 3060, 2921, 2853, 1710, 1639, 1593, 1529, 1458, 1311, 1241, 1180 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 12.80 (brs, 2H), 9.21 – 9.16 (m, 2H), 9.02 (d, *J* = 7.2 Hz, 2H), 8.62 – 8.49 (m, 2H), 8.49 – 8.38 (m, 2H), 4.48 (p, *J* = 7.3 Hz, 2H), 1.44 (d, *J* = 7.3 Hz, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm 174.42, 164.85, 156.88, 149.13, 137.01, 130.30, 121.04, 48.73, 17.33; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): *m/z* calculated for C₁₈H₁₈N₄O₆ [M+H]⁺: 387.1305, found: 387.1305.

2.3 Synthesis of Bipy-1

To a mixture of **Bipy-1-a** (1.0 g, 2.6 mmol), 1-Pyrenemethylamine hydrochloride (1.45 g, 5.4 mmol), HOBt·H₂O (0.70 g, 5.2 mmol) and EDC·HCl (1.49 g, 7.8 mmol) in CH₂Cl₂/DMF (4:1, 25 mL) was added TEA 2.2 mL at 0 °C. The reaction mixture was stirred for 1 h and was heated up to room temperature. After stirring for 2 days at room temperature, the solvent was removed by vacuum evaporation. The precipitate was filtered, washed with CH₂Cl₂, Ethanol, Diethyl ether and dried in vacuo to give (1.5 g, 71% yield) the pure solid. Decomposition 310 °C; IR (KBr pellet): 3273, 3043, 2975, 2927, 1920, 1789, 1621, 1592, 1534, 1457 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 9.25 – 9.18 (m, 2H), 8.97 (d, *J* = 7.2 Hz, 2H), 8.76 (t, *J* = 5.7 Hz, 2H), 8.54 (d, *J* = 8.3 Hz, 2H), 8.48 – 8.45 (m, 2H), 8.40 (d, *J* = 9.4 Hz, 2H), 8.36 – 8.21 (m, 8H), 8.21 – 8.02 (m, 8H), 5.18 – 5.03 (m, 4H), 4.64 (p, *J* = 7.1 Hz, 2H), 1.45 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm 172.67, 164.96, 156.80, 149.32, 137.16, 133.33, 131.26,

130.77, 130.51, 130.45, 128.45, 127.95, 127.86, 127.44, 126.77, 126.70, 125.69, 125.62, 125.18, 124.48, 124.39, 123.64, 120.88, 49.84, 18.45; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): m/z calculated for C₅₂H₄₀N₆O₄ [M+H]⁺: 813.3189, found: 813.3188.

2.4 Synthesis of Biphe-1-b

To a mixture of the Biphenyl-4,4'-dicarboxylic acid (**Biphe-1-c**) (1.0 g, 4.1 mmol), *D*-alanine methyl ester hydrochloride (1.21 g, 8.7 mmol), HOBt·H₂O (1.12 g, 8.3 mmol) and EDC·HCl (2.37 g, 12.4 mmol) in CH₂Cl₂/DMF (4:1, 25 mL) was added TEA 3.4 mL at 0 °C. The reaction mixture was stirred for 1 h and was heated up to room temperature. After stirring for 2 days at room temperature, the mixture was extracted with CH₂Cl₂ (3 x 30 mL). The combined organics were washed with brine, dried (Na₂SO₄), and concentrated. The resulting crude product was purified by recrystallization from CH₂Cl₂/ether to give a white solid, compound **Biphe-1-b** (1.1 g, 65%). mp. 220 °C; IR (KBr pellet): 3288, 3070, 2993, 2951, 1737, 1636, 1539, 1490, 1451, 1344, 1226, 1167, 1113, 1046 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ = 8.89 (d, *J* = 7.0 Hz, 2H), 8.08 - 7.97 (m, 4H), 7.88 (d, *J* = 6.6 Hz, 4H), 4.52 (p, *J* = 7.3 Hz, 2H), 3.67 (s, 6H), 1.44 (d, *J* = 7.3 Hz, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ = 173.64, 166.23, 142.33, 133.45, 128.66, 127.20, 52.38, 48.78, 17.23; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): *m/z* calculated for C₂₂H₂₄N₂O₆ [M+Na]⁺: 435.1527, found: 435.1531.

2.5 Synthesis of Biphe-1-a

A solution of **Biphe-1-b** (0.6 g, 1.5 mmol) in a mixture with EtOH (40 mL) was heated to reflux. The reaction mixture was then added to aqueous 1 M NaOH. After refluxing for 12 h, the organic solvents were removed in vacuo, and water (15 mL) was added. The remaining aqueous solution was acidified to pH 3 by adding 3 N HCl. The resulting precipitate was filtered and washed with water. The precipitate was dried under vacuum to give **Biphe-1-a** as a white solid in 78% yield. Decomposition 284 °C; IR (KBr pellet): 3302, 3065, 2853, 2640, 2534, 1717, 1636, 1540, 1490, 1457, 1378, 1319, 1241, 1176, 1116, 1042 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 8.74 (d, *J* = 7.2 Hz, 2H), 8.07 – 7.97 (m, 4H), 7.93 – 7.82 (m, 4H), 4.44 (p, *J* = 7.3 Hz, 2H), 1.42 (d, *J* = 7.3 Hz, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm 174.71, 166.15, 142.24, 133.71, 128.66, 127.15, 48.67, 17.38; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): *m/z* calculated for C₂₀H₂₀N₂O₆ [M+Na]⁺: 407.1214, found: 407.1218.

2.6 Synthesis of Biphe-1

To a mixture of **Biphe-1-a** (1.0 g, 2.6 mmol), 1-Pyrenemethylamine hydrochloride (1.46 g, 5.5 mmol), HOBt·H₂O (0.70 g, 5.2 mmol) and EDC·HCl (1.50 g, 7.8 mmol) in CH₂Cl₂/DMF (4:1, 25 mL) was added TEA 2.2 mL at 0 °C. The reaction mixture was stirred for 1 h and was heated up to room temperature. After stirring for 2 days at room temperature, the solvent was removed by vacuum evaporation. The precipitate was filtered, washed with CH₂Cl₂, Ethanol, Diethyl ether and dried in vacuo to give (1.4 g, 66% yield) the pure solid. Decomposition 302 °C; IR (KBr pellet): 3280, 3043, 2973, 2928, 1919, 1793, 1623, 1529, 1488, 1454 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 8.76 – 8.64 (m, 4H), 8.45 – 8.31 (m, 4H), 8.31 – 8.19 (m, 8H), 8.17 (s, 4H), 8.15 – 8.01 (m, 8H), 7.90 – 7.81 (m, 4H), 5.18 – 4.97 (m, 4H), 4.63 (p, *J* = 7.2 Hz, 2H), 1.44 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ ppm 172.94, 166.21, 142.18, 133.91, 133.37, 131.27, 130.78, 130.51, 128.80, 128.45, 127.95, 127.87, 127.43, 127.02, 126.78, 126.70, 125.69, 125.62, 125.17, 124.48, 124.39, 123.64, 49.78, 18.51; HRMS (ESI-TOF, positive mode, MeOH/H₂O 1:1): *m/z* calculated for C₅₄H₄₂N₄O₄ [M+H]⁺: 811.3279, found: 811.3279.

3. Supplementary scheme and figures



Scheme S1. The formation mechanisms of supramolecular polymers based on (A) Bipy-1 and (B) Biphe-1 in a mixed DMSO/H₂O.



Fig. S1 The morphology transformation of the self-assembled Bipy-1 upon addition of DMSO in a mixed DMSO/H₂O (1:99 v/v) on the mica; (A) DMSO/H₂O (1:99 v/v), (B) DMSO/H₂O (7:93 v/v), (C) DMSO/H₂O (16:84 v/v), (D) DMSO/H₂O (49:51 v/v). Scale bars, 250 nm.



Fig. S2 AFM images of supramolecular polymer II in DMSO/H₂O (50:50 v/v). Scale bars, 250 nm.



Fig. S3 CD and UV-vis spectra of (A, C) Bipy-1 (50 μM) and (B, D) Biphe-1 (50 μM) in a mixed DMSO/H₂O; monomeric ligand (black line), self-assembled excimer (blue line), exciplex (red line).



Fig. S4 AFM images of self-assembled Biphe-1 (A) in DMSO/H₂O (50:50 v/v) and (B) DMSO/H₂O (1:99 v/v). AFM cross-sectional analysis between the (C) green and (D) red dots in image A.



Fig. S5 (A) UV-vis and (B) PL spectra of Bipy-1 (50 μ M) in dimethyl sulfoxide (DMSO) at 25 °C. λ_{Ex} = 347nm.



Fig. S6 PL spectra of Bipy-1 at the concentration range of $1 \times 10^{-5} \sim 1 \times 10^{-4}$ M (interval: 1×10^{-5} M) (A) in DMSO/H₂O (50:50 v/v) and (B) DMSO/H₂O (1:99 v/v). (C) Plot for emission changes of Bipy-1 vs concentration at 470 nm in DMSO/H₂O (50:50 v/v) and (D) at 520 nm in DMSO/H₂O (1:99 v/v). λ_{Ex} = 347nm.



Fig. S7 Temperature-dependent UV spectra of self-assembled Bipy-1 (40 μ M) (A) with blue emission in DMSO/H₂O (50:50 v/v) and (B) with yellow emission in DMSO/H₂O (1:99 v/v) by heating. (C) Degree of aggregation of different concentrations of self-assembled Bipy-1 (A) with blue emission in DMSO/H₂O (50:50 v/v) and (B) with yellow emission in DMSO/H₂O (1:99 v/v) as a function of temperature at 360 nm.



Fig. S8 (A) Fluorescence spectral changes of self-assembled Bipy-1 (50 μ M) with exciplex structure upon addition of DMSO in a mixed DMSO/H₂O (1:99 v/v). (B) Photograph of self-assembled Bipy-1 upon addition of DMSO in a mixed DMSO/H₂O (1:99 v/v). λ_{Ex} = 347nm.



Fig. S9 (A) PL spectra of Biphe-1 (50 μ M) in a mixed DMSO/H₂O (fraction interval: 10 v/v in the range of 100:0 \rightarrow 70:30 v/v, then 5 v/v interval in the range of 70:30 \rightarrow 5:95 v/v). (B) Plot for maximum emission wavelength of Biphe-1 vs water content (%). (C) Photograph of self-assembled Biphe-1 in a mixed DMSO/H₂O (fraction interval: 10 v/v in the range of 100:0 \rightarrow 10:90 v/v, then 5 v/v interval in the range of 10:90 \rightarrow 1:99 v/v). λ_{Ex} = 347nm.



Fig. S10 (A) Fluorescence spectral changes of self-assembled Biphe-1 (50 μ M) with excimer structure upon addition of Bpy-COOH in a mixed DMSO/H₂O (5:95 v/v). (B) Photograph of self-assembled Biphe-1 (50 μ M) with excimer structure upon addition of Bpy-COOH in a mixed DMSO/H₂O (5:95 v/v). λ_{Ex} = 347nm.



Fig. S11 PL spectra of of Bipy-1 (50 μ M) in a mixed DMSO and other solvent system (1:99 v/v). λ_{Ex} = 347nm.



Fig. S12 FT-IR spectra of C=O stretching vibration of monomeric Bipy-1 (black line), self-assembled exciplex (yellow line), and excimer (blue line).



Scheme S2. A pictorial representation of different self-assembly modes depending on solvent property.



Fig. S13 Powder XRD pattern of self-assembled Bipy-1; (A) excimer and (B) exciplex.

<i>C</i> (M)	<i>T_e</i> (K)	ΔH_e (kJ mol ⁻¹)	Ka	$< N_{\rm n}({\rm T_e})>$
1.0 × 10 -4	361.51	-55.134	4.0 x 10 ⁻³	6.2
8.0 × 10 ⁻⁵	360.01	-52.241	4.9 x 10 ⁻³	5.9
6.0 x 10 ⁻⁵	358.71	-39.150	5.3 x 10 ⁻³	5.7
4.0 × 10 ⁻⁵	356.62	-35.130	6.9 x 10 ⁻³	5.2

Table S1. Thermodynamic Parameters of excimer.

4. Analytic data

4.1 ¹H-NMR and ¹³C-NMR spectoscopy



Fig. S14 ¹H NMR spectrum (300 MHz) of Bipy-1-a in DMSO-*d*₆ at 25 °C.



Fig. S15 ¹³C NMR spectrum (75 MHz) of Bipy-1-a in DMSO- d_6 at 25 °C.



Fig. S16 ¹H NMR spectrum (300 MHz) of Bipy-1 in DMSO- d_6 at 25 °C.



Fig. S17 ¹³C NMR spectrum (75 MHz) of Bipy-1 in DMSO- d_6 at 25 °C.



Fig. S18 ¹H NMR spectrum (300 MHz) of Biphe-1-b in DMSO- d_6 at 25 °C.



Fig. S19 ¹³C NMR spectrum (75 MHz) of Biphe-1-b in DMSO- d_6 at 25 °C.



Fig. S20 ¹H NMR spectrum (300 MHz) of Biphe-**1-a** in DMSO- d_6 at 25 °C.



Fig. S21 ¹³C NMR spectrum (75 MHz) of Biphe-1-a in DMSO- d_6 at 25 °C.



Fig. S22 ¹H NMR spectrum (300 MHz) of Biphe-1 in DMSO-*d*₆ at 25 °C.



Fig. S23 ¹³C NMR spectrum (75 MHz) of Biphe-1 in DMSO- d_6 at 25 °C.

4.2 HR ESI-MS spectrometry



Fig. S24 HR ESI-MS spectrum of Bipy-1-a in MeOH.



Fig. S25 HR ESI-MS spectrum of Bipy-1 in MeOH.



Fig. S26 HR ESI-MS spectrum of Biphe-1-b in MeOH.



Fig. S27 HR ESI-MS spectrum of Biphe-1-a in MeOH.



