

Supporting information for

**Alignment of supramolecular J-aggregates based on uracil-functionalized
BODIPY dye for polarized photoluminescence**

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1. General methods

Chemicals and Reagents: All the chemicals were commercially available and used without further purification unless otherwise stated. Anhydrous dichloromethane (DCM) was distilled over CaH₂ and THF was distilled over sodium and stored under Argon. Products were purified by column chromatography with silica gel (300-400 mesh).

NMR spectroscopy: ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD (400 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. Multiplicities for proton signals are abbreviated as *s*, *d*, *t*, *q*, *p* and *m* for singlet, doublet, triplet, quartet, pentet and multiplet, respectively.

Mass spectrometry: Mass spectra were measured on a Bruker Daltonics Autoflex tof/tof III.

UV/Vis spectroscopy: UV/Vis absorption spectra were recorded on an Agilent Technologies Cary 300 UV/Vis spectrophotometer equipped with a SPV 1×1 temperature controller. The solvents for spectroscopic studies were spectroscopic grade. The spectra were recorded in quartz cuvettes and the extinction coefficients ϵ was calculated according to Lambert-Beer's law.

Fluorescence spectroscopy: The steady state and time-resolved fluorescence spectra were measured on Edinburgh FLS980 spectrofluorometer. All the fluorescence spectra were corrected. Fluorescence quantum yields were determined on a Hamamatsu C11347-12 Quantaaurus-QY Absolute PL quantum yield spectrometer. Fluorescence polarization measurement was performed on the Edinburgh FLS980 spectrofluorometer equipped with linear polarizers in incident light path and detection light path. For the excitation polarization measurement, a polarizer was placed in the excitation light path while the emission polarizer was removed. The excitation polarizer can be rotated to be parallel or perpendicular to the ground. On the contrary, the polarized photoluminescence was measured by exciting the thin film of **1** with unpolarized light and detecting the fluorescence at different positions of emission polarizer. The emission polarizer can also be rotated to have different angles with respect to the ground. The rubbed thin film of **1** on quartz wafer was placed on a specimen holder in spectrofluorometer with rubbing direction perpendicular to the ground. Time-resolved fluorescence decay spectra were measured on the Edinburgh FLS980 spectrofluorometer equipped with an nF920 Nanosecond Flashlamp as light source. The fluorescence decay were measured at a pulse width < 1ns and repetition rate of 10 MHz.

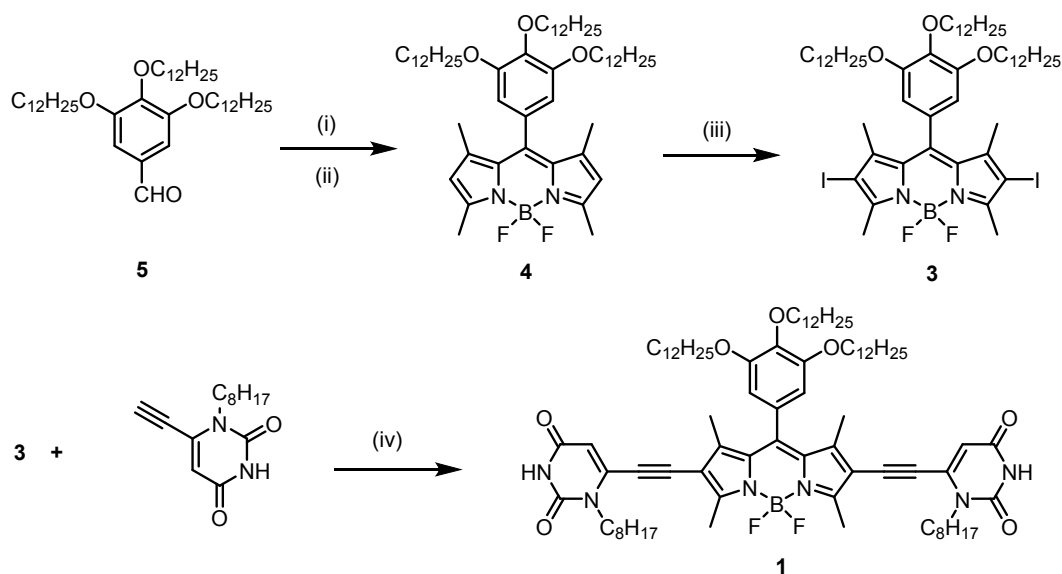
Transmission electron microscopy: Transmission electron microscopy (TEM) measurements were performed on a Hitachi HT7700 transmission electron microscope, operating at an acceleration voltage of 80 kV. For the observation of aggregates, 400-mesh copper grids coated with carbon was dipped in a drop of sample solution of dye **1**. About 2 min after the deposition, the grid was placed

on filter paper to remove solvent. Staining was performed by a drop of uranyl acetate aqueous solution (0.5 % wt) onto the copper grid. After 1 min, the liquid on the grid was removed with filter paper.

Atomic force microscopy: AFM measurements were performed under ambient conditions using an NT-MDT NTEGRA spectra system operating in tapping mode. Silicon cantilevers with a resonance frequency of ~300 kHz were used. The sample for AFM observation was prepared by drop-casting the MCH solution of dye **1** on mica surface and evaporating the solvent.

Preparation of J-aggregate solution and aligned thin film of dye 1: The powder of dye **1** (3.4 mg) was placed in a volumetric flask (100 mL) followed by addition of *ca.* 80 mL MCH. Then the flask was disposed with ultrasonic bath (180 W) for 30 min until the dye **1** was completely dissolved and a blue solution was obtained. Further adding MCH to 100 mL gave the stock solution of J-aggregates of **1** ($c = 2.5 \times 10^{-5}$ M). The formation of J-aggregates was confirmed by UV/Vis absorption spectra. The dye **1** solution in MCH ($c = 2.5 \times 10^{-5}$ M) was firstly spin-casted on quartz wafer. After evaporating the solvent, a thin film of solid **1** was formed on the surface of quartz wafer. Then the thin film was rubbed using a commercial buffing machine with a friction cylinder rotating at rate of 2000 rpm, while the quartz wafer deposited with **1** thin film was translated laterally at a rate of 10 mm/s. The friction cylinder was wrapped with polyacrylonitrile fibrous cloth. This operation follows the common friction method as employed in previous publications.^[1] The rubbed film was used for fluorescence polarization measurements.

2. Synthesis and characterization of BODIPY dye 1



Scheme S1. Synthetic route of BODIPY dye 1. Reagents and conditions: (i) 2,4-dimethylpyrrole, CF_3COOH , CH_2Cl_2 , DDQ, r.t., 2 h; (ii) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, triethylamine, r.t., 30%; (iii) I_2 , HIO_3 , EtOH , H_2O , 6 h, 72%; (iv) $\text{Pd}(\text{PPh}_3)_4$, CuI , Et_3N , 6 h, 57% - 60%.

Compound 4: 3,4,5-Tris(dodecyloxy)benzaldehyde^[2] (compound 5) (1.3 g, 2.0 mmol) and 2,4-dimethylpyrrole (0.4 mL, 4.0 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL) under Ar. After stirring for 15 min, 0.036 mL TFA was added and the reaction was continued at room temperature for about 2 h. After the complete consumption of compound 5 (monitored by TLC), DDQ (8.5 mmol, 2.0 g) was added into the reaction mixture. After stirring for 2 h, triethylamine (10.0 mL, 57 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10.0 mL, 79 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 10 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{n-hexane} = 1/1$, v/v) to give an orange-colored viscous substance (0.53 g, 30%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , 300K, TMS): $\delta = 6.47$ (s, 2H), 5.99 (s, 2H), 3.96 (qd, $J = 19.54$), 2.55 (s, 6H), 1.87-1.70 (m, 6H), 1.53 (s, 6H), 1.49-1.39 (m, 6H), 1.26 (m, 48H), 0.89 (m, 9H).

Compound 3: A mixture of compound 4 (877.15 mg, 1.0 mmol) and I_2 (317.5 mg, 2.5 mmol) dissolved in $\text{C}_2\text{H}_5\text{OH}$ (20 mL) was stirred at room temperature, a concentrated aqueous solution of HIO_3 (352mg, 2 mmol) was added dropwisely to reaction system. The reaction was carried out at 60°C for 4 h. The residue obtained after the removal of the solvent by rotary evaporation was extracted with ethyl acetate and washed with saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (3×20 mL) and water (3×30 ml), then dried with anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was further purified using column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{Hexane} = 1/2$, v/v) to afford 3 (812.9 mg, 72% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = 6.42$ (s, 2H), 4.03 (t, $J = 8$ Hz, 2H),

3.91 (t, $J = 8$ Hz, 4H), 2.64 (s, 6H), 1.80-1.75 (m, 6H), 1.55 (d, $J = 4$ Hz, 10H), 1.49-1.41 (m, 4H), 1.30-1.26 (m, 46H), 0.89-0.86 (m, 9H).

Compound 1: Copper(I) iodide (0.02 mmol, 3.8 mg), Pd(PPh₃)₄ (0.02 mmol, 23 mg) and 6-ethynyl-1-n-octyluracil (0.4 mmol, 99.6 mg) were added to compound **3** (0.2 mmol, 225.8 mg) under inert atmosphere. Triethylamine (5 mL) was added to this mixture via a syringe. After reacting for 6h at 80 °C (oil bath), the completion of the reaction was monitored by TLC. The reaction was quenched by addition of water (20 mL). The product was extracted with diethyl ether (3×40 mL). The combined organic layers were then washed with H₂O (3×40 mL) and dried (MgSO₄) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with methanol/dichloromethane (1:30, v/v) as eluent. Dye **1** (156.1 mg, 60% yield) was recrystallized from hexane and obtained as purple crystals. ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 8.03$ (s, 2H), 7.42 (s, 2H), 6.44 (s, 2H), 4.01 (t, $J = 4$ Hz, 2H), 3.91 (t, $J = 4$ Hz, 4H), 3.74 (t, $J = 8$ Hz, 4H), 2.67 (s, 6H), 1.81-1.77 (m, 6H), 1.75-1.71 (m, 4H), 1.66 (s, 6H), 1.54 (s, 8H), 1.45-1.26 (m, 66H), 0.89-0.86 (m, 15H). ¹³C NMR (101 MHz, CDCl₃, ppm): $\delta = 161.05, 154.37, 149.42, 145.70, 128.75, 106.12, 100.29, 86.66, 77.22, 73.86, 69.59, 49.38, 31.93, 31.70, 30.33, 29.78, 29.71, 29.66, 29.62, 29.42, 29.36, 29.15, 29.08, 26.38, 26.16, 26.06, 22.69, 22.58, 14.11, 14.04, 13.75, 13.44$. MS (MALDI-TOF): calculated for C₈₃H₁₂₈BF₂N₆O₇, [M + H]⁺ = 1370.994 m/z, found 1371.121 m/z. Elemental analysis: Anal. calcd for C₈₃H₁₂₈BF₂N₆O₇: C 72.78 %, H 9.35%, N 6.14%; found: C 72.42%, H 9.45%, N 5.98%. UV/Vis (CHCl₃): $\lambda_{\max} = 559$ nm, $\epsilon = 8.3 \times 10^4$ M⁻¹ cm⁻¹; Fluorescence (CHCl₃): $\lambda_{\text{Em}} = 578$ nm.

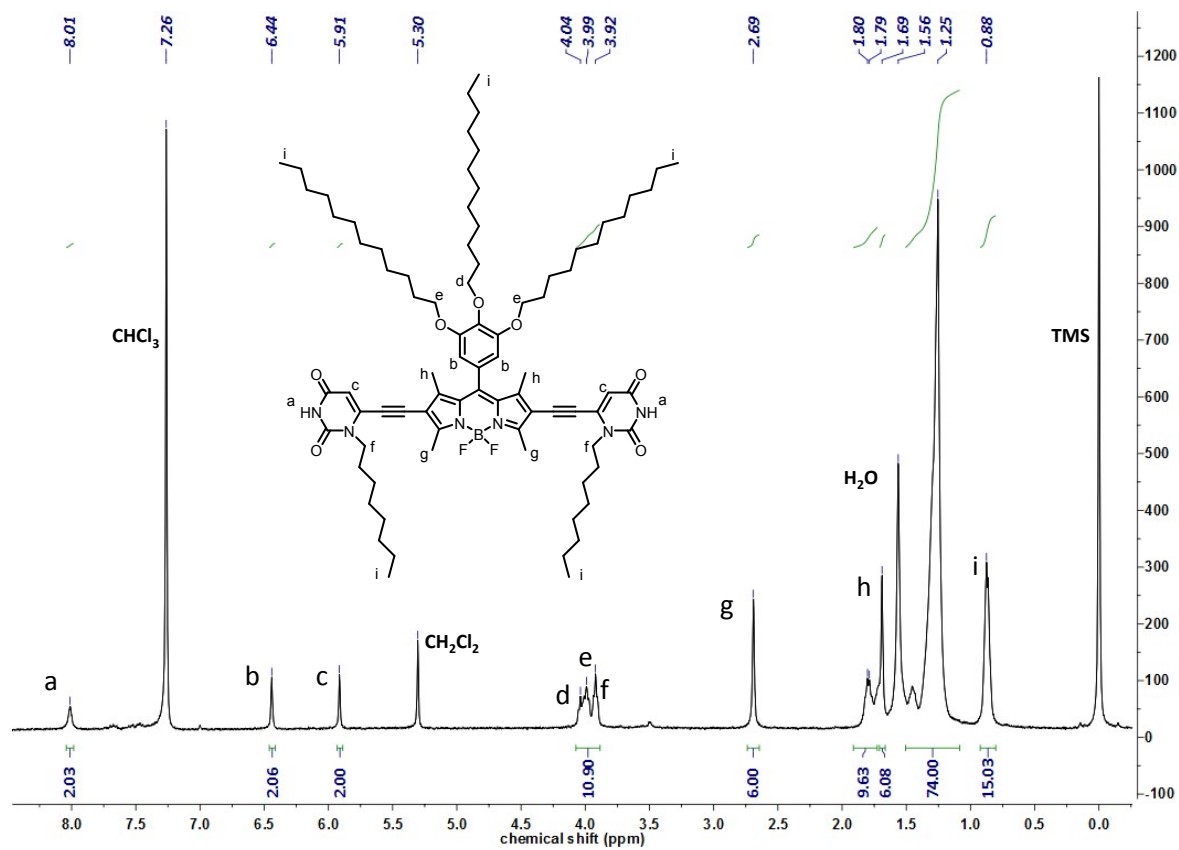


Figure S1. ¹H NMR spectra (400 MHz, CDCl₃) and signal assignments of BODIPY dye 1.

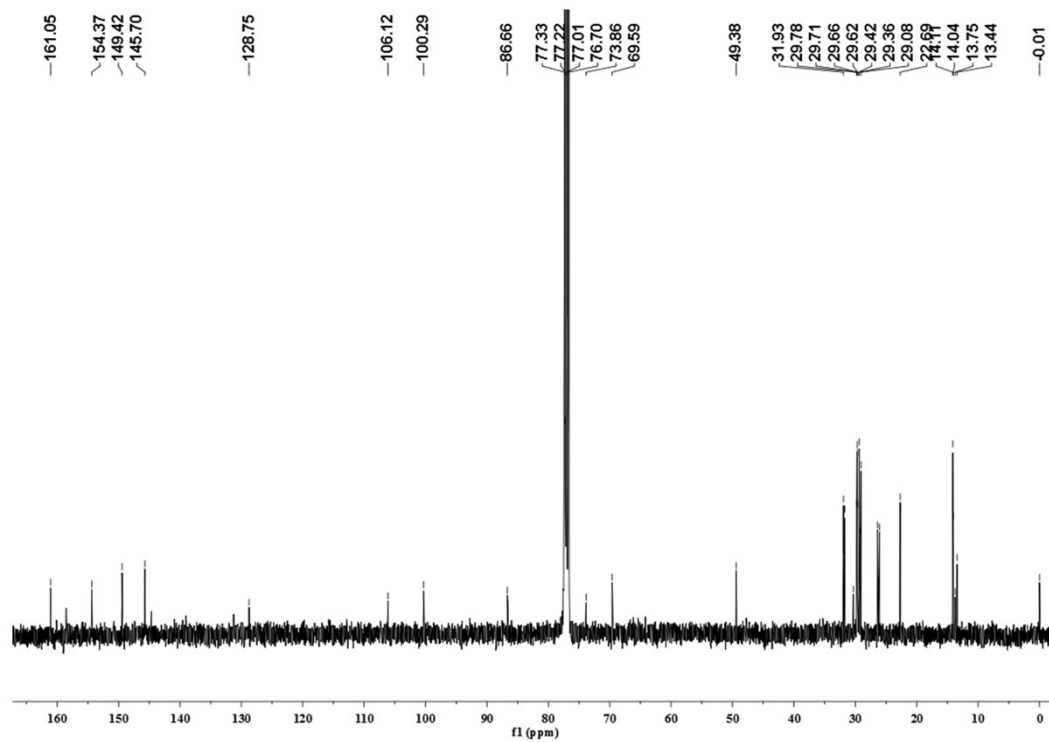


Figure S2. ¹³C NMR spectra (101 MHz, CDCl₃) of BODIPY dye 1

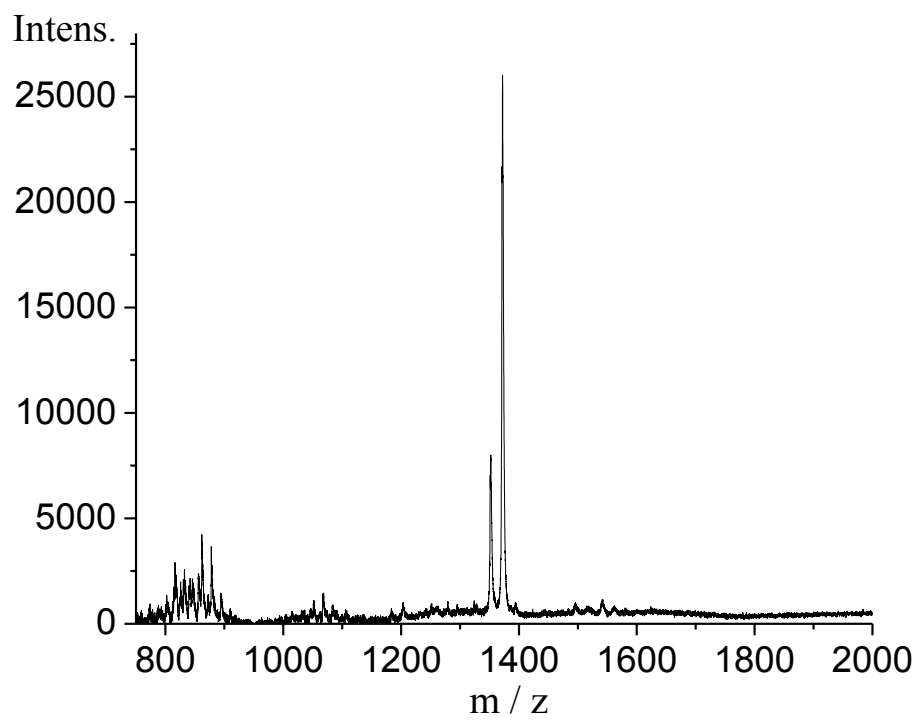


Figure S3. Mass spectrum (MALDI-TOF) of BODIPY dye 1

3. Studies on supramolecular polymerization of dye 1

3.1 Temperature-dependent UV/Vis absorption spectroscopic study

The molar fraction of aggregated molecules (α_{agg}) in solution can be estimated from the UV/Vis absorption spectra based on the assumption that the dye molecules are completely accommodated in aggregates ($\alpha_{agg} = 1$) at lowest temperature (or highest concentration) while they exist as monomers ($\alpha_{mon} = 1$) at highest temperature (or lowest concentration). The absorption at a certain wavelength can be considered as summing the absorptions of monomers and aggregates (Eq. S1). Because the summation of the fractions of monomer and aggregated molecules equals unity (Eq. S2), the fraction of aggregated molecules can be calculated by solving the equations set of Eq. S1 and S2.

$$\epsilon(559\text{nm}) = \epsilon_{mon}(559\text{nm})\alpha_{mon} + \epsilon_{agg}(559\text{nm})\alpha_{agg} \quad \text{S1}$$

$$\alpha_{mon} + \alpha_{agg} = 1 \quad \text{S2}$$

Temperature-dependent aggregation process can be fitted by the nucleation-elongation model proposed by Meijer et al.^[3] In the elongation regime, the fraction of aggregated molecules α_{agg} is given by Eq. S3, in which the ΔH_e is the molar enthalpy release due to noncovalent interactions during elongation, T_e is the critical elongation temperature, α_{sat} is a parameter introduced to ensure that $\alpha_{agg}/\alpha_{sat}$ does not exceed unity.

$$\alpha_{agg} = \alpha_{sat} \left(1 - \exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad \text{S3}$$

At the temperatures above T_e (nucleation regime), the fraction of aggregated molecules in the nucleation regime can be described as Eq. S4, in which K_a is the dimensionless equilibrium constant of the activation step at T_e . A higher degree of cooperativity is expressed in a smaller K_a value.

$$\alpha_{agg} = K_a^{1/3} \exp \left[\frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \left[\frac{2}{3} K_a^{-1/3} - 1 \right] \quad \text{S4}$$

The plots of α_{agg} versus temperature estimated from temperature-dependent UV/Vis absorption spectra of dye 1 was fitted with the above model and the thermodynamic parameters for the J-aggregation of dye 1 is summarized in Table S1. The experimental results for the heating process is shown in the main text. Fitting results for the cooling process (Figure S4) derived a critical

temperature of 354 K (very close to the 355 K of the heating cycle), which indicated that the formation of J-aggregates is nearly reversible with very slight thermal hysteresis.

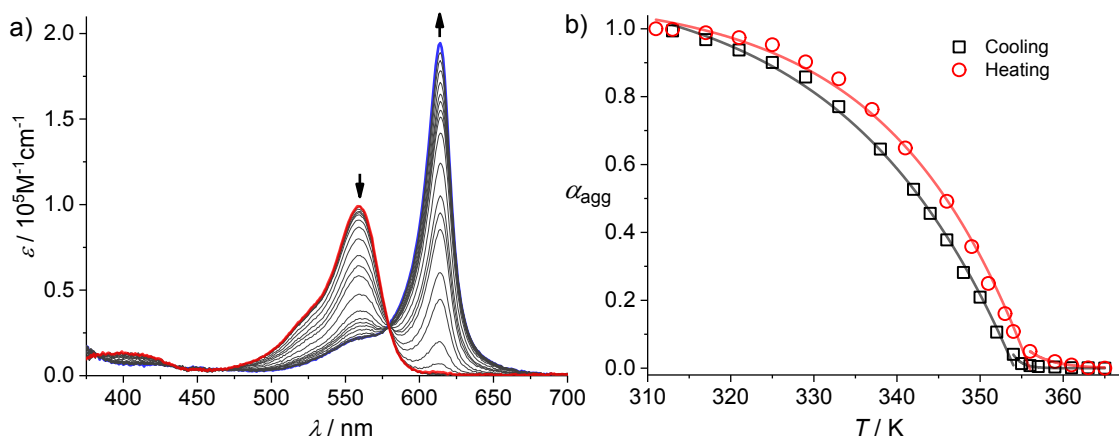


Figure S4. a) Temperature-dependent UV/Vis absorption spectra of BODIPY **1** in MCH ($c_T = 3.0 \times 10^{-7}$ M) at a cooling rate of 0.5 K/min. The arrows indicate the spectra changing at 559 nm and 611 nm with decreasing temperature from 365 to 303 K; b) Plot of molar fraction of aggregated **1** as a function of temperature for heating and cooling processes and the fitting curves applying cooperative self-assembly model.

Table S1. The critical elongation temperature (T_e), molar enthalpy (ΔH_e) and dimensionless equilibrium constant (K_a) obtained from fitting of $\alpha_{agg} - T$ plots for heating and cooling processes of J-aggregation of dye **1** at $c_T = 3.0 \times 10^{-7}$ M

Process	T_e / K	ΔH_e / kJ mol ⁻¹	K_a
Heating	355	-70	1.4×10^{-3}
Cooling	354	-53	1.1×10^{-3}

3.2 Concentration-dependent UV/Vis absorption spectroscopic study

Concentration-dependent aggregation process can be fitted by the Goldstein-Stryer model^[4] which describes the cooperative supramolecular polymerization based on the assumption that the size of polymer changes only by monomer association and dissociation. A nucleation step (with equilibrium constant K_s) is considered prior to the elongation (with equilibrium constant K_E) of the aggregates. In the low concentration range ($c_T < 1/K_E$), only oligomers with size smaller than s are formed which are in pre-equilibrium with monomers. Once the concentration exceeds $1/K_E$, elongated polymers are formed and the fraction of aggregated molecules (α_{agg}) increases drastically with the increase of concentration. The relationship between dimensionless total concentration $K_E c_T$ and monomer concentration $K_E c_M$ can be described by Eq. S5, in which σ is the cooperativity factor defined as $\sigma = K_s / K_E$.

$$K_E c_T = \frac{s(K_E c_M)^s \sigma^{s-1}}{1 - K_E c_M} + \frac{(K_E c_M)^{s+1} \sigma^{s-1}}{(1 - K_E c_M)^2} + \frac{K_E c_M (s(\sigma K_E c_M)^{s-1} - 1)}{\sigma K_E c_M - 1} - \frac{\sigma (K_E c_M)^2 ((\sigma K_E c_M)^{s-1} - 1)}{(\sigma K_E c_M - 1)^2}$$

S5

Consequently, α_{agg} can be calculated from Eq. S6.

$$\alpha_{agg} = 1 - \alpha_{mon} = 1 - (K_E c_M) / (K_E c_T) \quad S6$$

By calculating $K_E c_T$ from the data of $K_E c_M$ ($K_E c_M < 1$), the curve of α_{agg} versus $K_E c_T$ can be drawn. The experimental data of α_{agg} evaluated from UV/Vis spectra were collected and manually fitted with calculated curves for the optimal match. The fitting results and the derived parameters s , σ and K_E are shown in Figure S4.

The concentration-dependent UV/Vis absorption spectroscopic experiments were performed at higher temperatures of 358, 363, and 368 K (Figure S5), because no disaggregation could be detected upon diluting the MCH solution to a concentration of 1.0×10^{-7} M at room temperature. By manually fitting the experimental data with Goldstein-Stryer model, the nucleus size s of 2 and cooperativity factor σ of 0.004 - 0.006 were obtained, along with the elongation equilibrium constants of K_E at different temperatures (Table S2).

The standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) can be determined from the linear relationship in van't Hoff plot applying Eq.S7 in which R is the ideal gas constant.

$$\ln K_E = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad S7$$

The van't Hoff plot exhibits a good linear relationship between $\ln K_E$ and $1/T$ (Figure S5) from which the standard enthalpy (ΔH°) and entropy (ΔS°) were estimated to be -57 kJ mol^{-1} and $-38 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. As a consequence, the equilibrium constant of aggregation at room temperature can be derived as $K_E(298\text{K}) = 9.80 \times 10^7 \text{ M}^{-1}$ by extrapolation method.

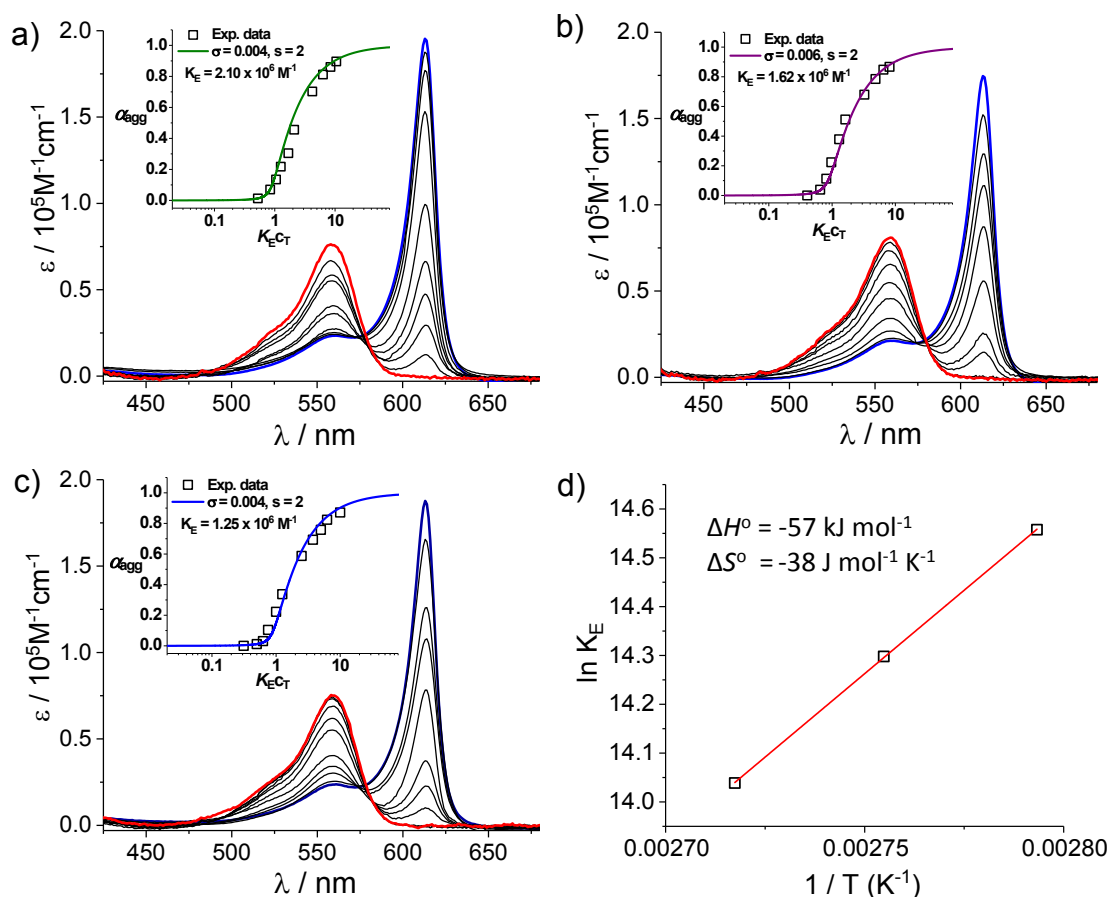


Figure S5 UV/Vis absorption spectra of BODIPY **1** in different concentrations of MCH solution ($8.0 \times 10^{-6} \text{ M}$ to $2.5 \times 10^{-7} \text{ M}$) at a) 358 K, b) 363 K, and c) 368 K; Insets: plots of molar fraction of aggregated molecules versus dimensionless concentration $K_E C_T$ and fitting curves applying Goldstein-Stryer model. d) Natural logarithm of K_E ($\ln K_E$) as a function of reciprocal temperature ($1/T$) showing a linear relationship.

Table S2. Thermodynamic parameters for the J-aggregation of dye **1** obtained from fitting of concentration-dependent aggregation processes with Goldstein-Stryer model and analysis of van't Hoff plot.

T / K	s	σ	$K_N / 10^3 \text{ M}^{-1}$	$K_E / 10^6 \text{ M}^{-1}$
358	2	0.004	8.40	2.10
363	2	0.006	9.72	1.62
368	2	0.004	5.00	1.25

3.3 Fluorescence studies

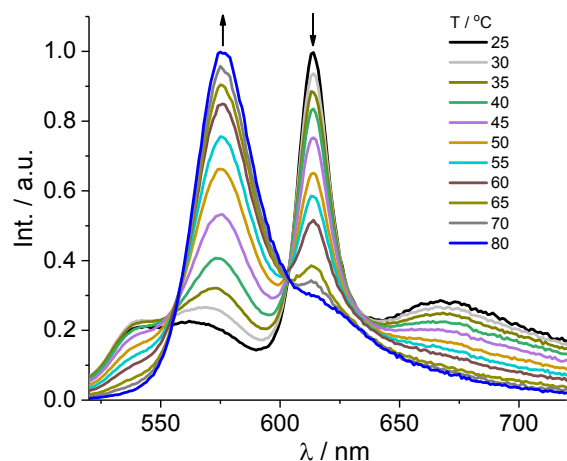


Figure S6. Normalized fluorescence spectra of **1** in MCH ($c_T = 3.0 \times 10^{-7}$ M) at different temperatures ($\lambda_{Ex} = 350$ nm). The arrows indicate the change of emission band with increasing temperature.

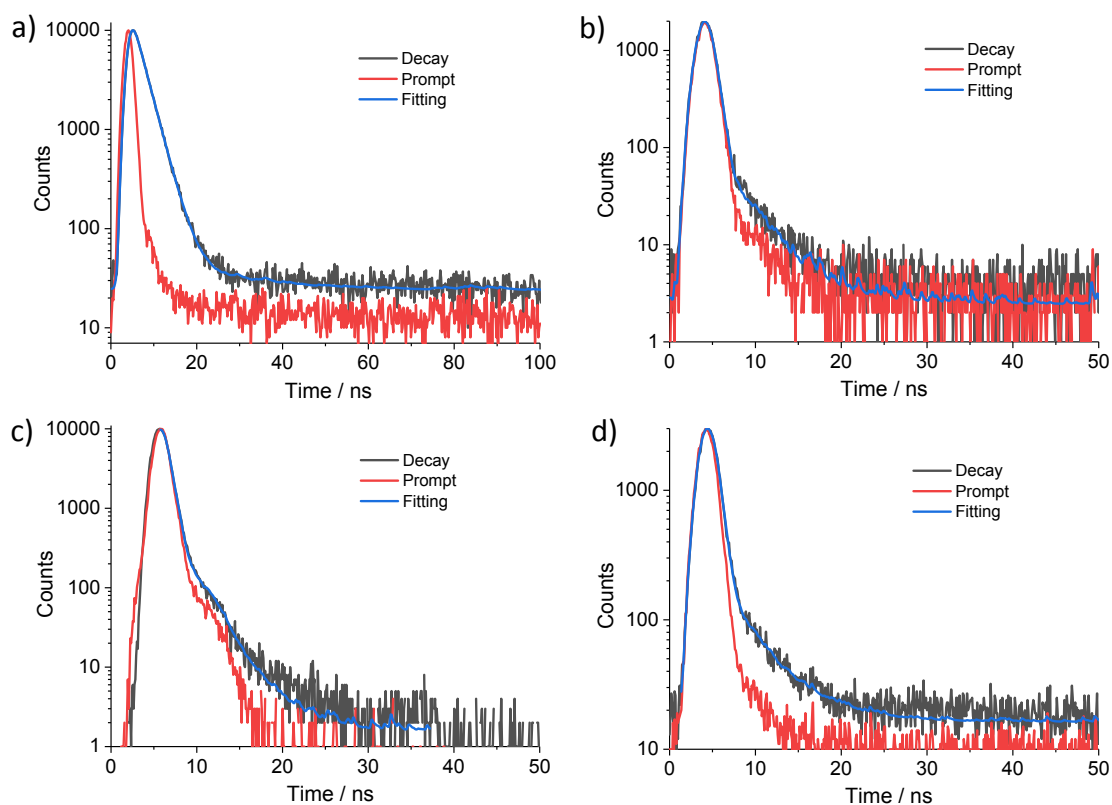


Figure S7. a) Fluorescence decay curves of monomer **1** in MCH measured at 40°C (collected emission wavelength $\lambda_{Em} = 576$ nm); Fluorescence decay curves of J-aggregates of **1** b) in MCH solution ($\lambda_{Em} = 616$ nm) and c) in rubbed thin film ($\lambda_{Em} = 612$ nm). d) Fluorescence decay curves of J-aggregates of **1** collected at $\lambda_{Em} = 670$ nm. All spectra were measured at excitation wavelength of $\lambda_{Ex} = 350$ nm.

Table S3. Photophysical parameters for monomers and J-aggregates of dye **1**.

Species	Φ^a	$\lambda_{Em}^b / \text{nm}$	τ^c / ns	τ_1^d / ns	τ_2^d / ns	$^e k_f / \text{s}^{-1}$	$^f k_{nr} / \text{s}^{-1}$
Monomers ^g	0.29	576	3.66	3.48 (98.54%)	15.98 (1.46%)	7.92×10^7	1.94×10^8
J-aggregates ^g	0.13	616	0.41 ^h	0.23 (95.35%)	4.18 (4.65%)	3.17×10^8	2.12×10^9
J-aggregates ^g	0.13	616	0.59 ⁱ	0.23 (89.84%)	3.75 (10.16%)	—	—
Film	0.17	612	0.40	0.22 (95.43%)	4.16 (4.57%)	4.25×10^8	2.07×10^9

^a Fluorescence quantum yields.

^b Wavelength of emission maximum.

^c Averaged fluorescence lifetimes measured at excitation wavelength of $\lambda_{Ex} = 350 \text{ nm}$.

^d Components of bi-exponential fluorescence lifetimes and pre-exponential factors (in brackets).

^e $k_f = \Phi / \tau$.

^f $k_{nr} = k_f * (1 / \Phi - 1)$.

^g Measured in MCH solutions.

^h Monitored at $\lambda = 616 \text{ nm}$.

ⁱ Monitored at $\lambda = 670 \text{ nm}$.

3.4 Studies on intermolecular H-bonding interactions

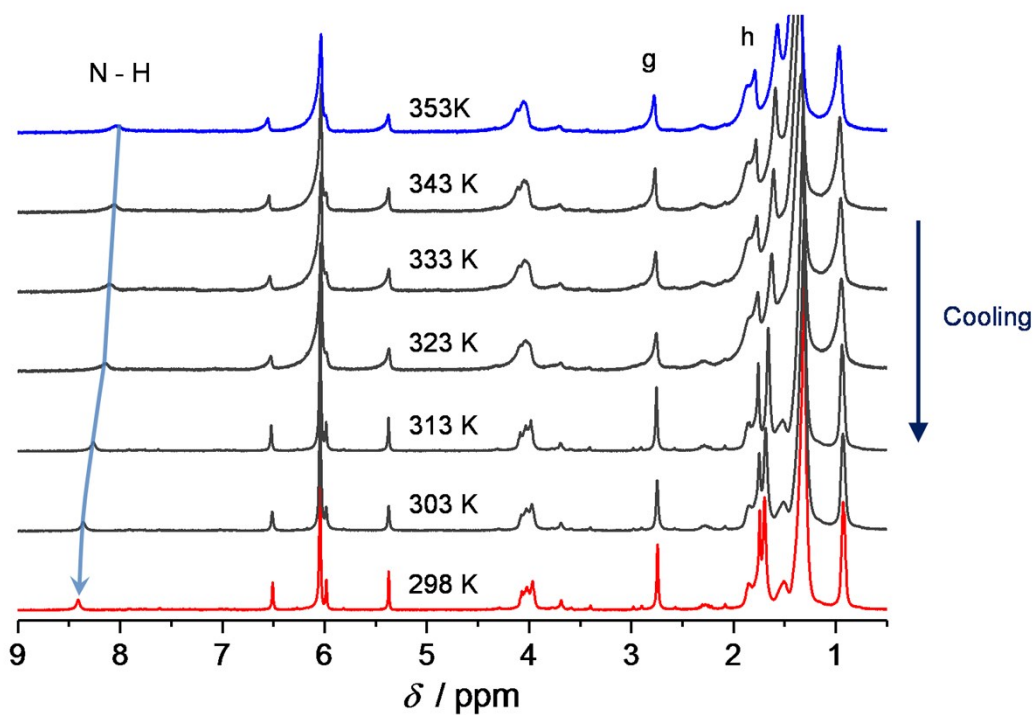


Figure S8. Temperature-dependent ¹H NMR spectra of dye **1** in 1,1,2,2-tetrachloroethane-D₂ (TCE-D₂) at a concentration of 5 × 10⁻³ M.

3.5 Morphological study

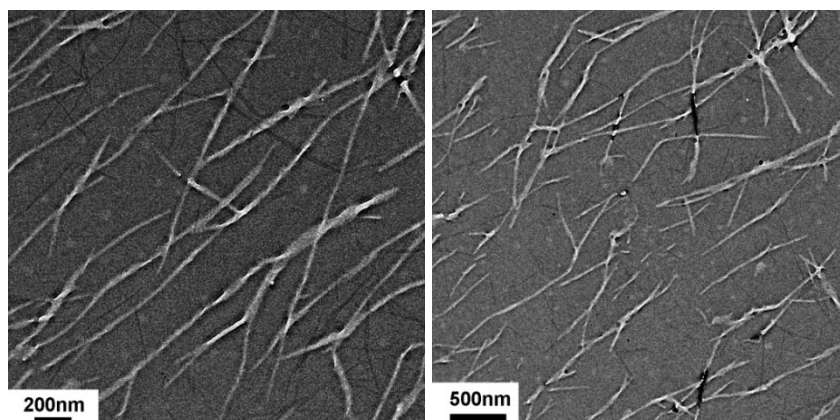


Figure S9. TEM images of J-aggregates of **1** in MCH ($c_T = 1.0 \times 10^{-5}$ M)

3.6 Excitation polarization studies

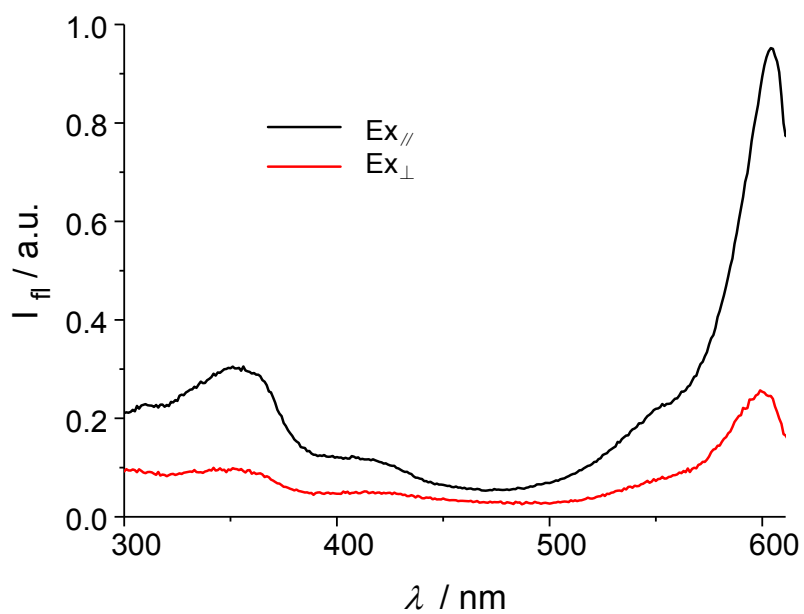


Figure S10. Excitation spectra ($\lambda_{\text{Em}} = 618 \text{ nm}$) of rubbed **1** thin film by setting the excitation polarizer parallel (black) / perpendicular (red) to the rubbing direction of the film while removing emission polarizer out of the light path.

4. Calculation of the spectral shift applying Kasha's excitonic coupling theory

The UV/Vis absorption spectroscopy showed a large bathochromic shift for the absorption band of J-aggregates comparing with the monomeric states of dye **1**. This significant spectral shift can be speculated to arise from the excitonic coupling between transition dipole moments of neighboring dye molecules stacking in a slipped fashion, which is described by Kasha's exciton model^[5]. The transition dipole moment of the monomer can be calculated from integrating the reduced UV/Vis absorption spectra according to Eq. 8, in which h is the Planck's constant (6.626×10^{-34} Js), c the speed of light (2.998×10^8 m/s), ε_0 the dielectric constant of vacuum (8.854×10^{-12} F/m), $\varepsilon(\tilde{\nu})$ the molar extinction coefficient at wavenumber of $\tilde{\nu}$, N_A the Avogadro's number (6.022×10^{23} mol⁻¹).

$$|\mu_{eg}|^2 = \frac{3hc\varepsilon_0 \ln 10}{2\pi^2 N_A} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} \quad \text{S8}$$

As a result, the transition dipole moment was calculated as $|\mu_{eg}| = 7.9$ D.

The exciton splitting J caused by the interaction between parallel arranged neighboring molecules in aggregates can be calculated by Eq. S9, where r_{uv} is the distance between the centers of two neighboring molecules, θ the slip angle resulting from the translational offset of these two molecules.

$$J = \frac{|\mu_{eg}|^2}{4\pi\varepsilon_0 r_{uv}^3} (1 - 3\cos^2\theta) \quad \text{S9}$$

Then the transition energy for aggregate can be expressed as Eq. S10,^[6] in which ΔE_{mon} is the transition energy for the isolated monomer, ΔE_{vdW} is the difference in van der Waals interaction energy between ground state of a molecule and the excited state of its neighbor molecule, and J_i represent the exciton splitting caused by interactions between neighboring molecules in aggregate.

$$\Delta E_{\text{agg}} = \Delta E_{\text{mon}} + \Delta E_{\text{vdW}} + \sum J_i \quad \text{S10}$$

Thus the spectra shift $\Delta\tilde{\nu}_{\text{agg-mon}}$ of the aggregate absorption band with respect to the monomer absorption band can be estimated as Eq. S11.

$$\Delta\tilde{\nu}_{\text{agg-mon}} = (\Delta E_{\text{agg}} - \Delta E_{\text{mon}}) / hc = \Delta E_{\text{vdW}} / hc + (\sum J_i) / hc. \quad \text{S11}$$

Since ΔE_{vdW} is a negative value which cannot be determined, the evaluation of spectral shift can be simplified as:

$$\Delta\tilde{\nu}_{\text{agg-mon}} < (\Sigma J_i) / hc. \quad \text{S12}$$

By assuming that the ΣJ_i is contributed by J_π (interaction between neighboring molecules in π - π stacking direction) and J_H (interaction between neighboring molecules in H-bond direction), $\Delta\tilde{\nu}_{\text{agg-mon}}$ can be evaluated by Eq. S13 for m nearest neighboring molecules in π - π stacking direction and n nearest neighboring molecules in H-bond direction.

$$\Delta\tilde{\nu}_{\text{agg-mon}} < m J_\pi / hc + n J_H / hc \quad \text{S13}$$

As a result, the spectral shift is determined by the values of distances between chromophore centers in H-bond direction (r_H) and π - π stacking direction (r_π) as well as the slip angles resulting from translational offset for two H-bonded molecules (θ_H) and two π - π stacked molecules (θ_π) with respect to the aggregation direction. When the values of distances were set as $r_H = 2.4$ nm and $r_\pi = 0.8$ nm, and the slip angles were set as $\theta_H = 10^\circ$ and $\theta_\pi = 34^\circ$, the exciton splitting for interactions in π - π stacking direction can be evaluated as $J_\pi / hc = -646$ cm^{-1} , while that for interactions in H-bond direction is evaluated as $J_H / hc = -42$ cm^{-1} . Thus the calculation with Eq. S13 provides an estimated spectral shift of $\Delta\tilde{\nu}_{\text{agg-mon}} \leq -1376$ cm^{-1} for brickwork arrangement ($m = 2, n = 2$) of dye molecules, in good agreement with experimental data of $\Delta\tilde{\nu}_{\text{exp}} = -1496$ cm^{-1} obtained from UV/Vis measurements.

5. References

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