Supporting Information

Optical and Structural Properties of ESIPT Inspired HBT–Fluorene Molecular Aggregates and Liquid Crystals

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Details about X-ray single crystal experiments for Ia and Ib.

Supporting References

Experimental

Materials & Characterization methods

Phosphorus trichloride, 4-bromo-2-hydroxybenzoic acid, 2-aminothiophenol, 2,7–dibromo-9,9-dihexylfluorene, 2,7-dibromo-9,9-dioctylfluorene, 1,3-propanediol, *n*-BuLi, Pd(PPh₃)₄, K₂CO₃, NaH, BBr₃, methyl iodide, and trimethylborate were purchased from Tokyo Chemical Industries (TCI), Japan. All the solvents used for the synthesis were from Wako Pure Chemical Industries Ltd., Japan. All the reagents were used without further purification.

The intermediates and compounds were characterized by ¹H NMR and ¹³C NMR spectroscopy, and MALDI-TOF (Matrix-assisted laser desorption ionization time-of-flight) and APCI (Atmospheric pressure chemical ionization) -MS spectrometry. The ¹H NMR spectra were recorded on a JEOL 400SS (400 MHz) spectrometer and ¹³C NMR spectra on a JEOL 400SS (100 MHz) spectrometer, and all spectra were recorded in a CDCl₃ & THF- d_8 solvents using TMS as an internal reference standard at room temperature (20°C). Chemical shifts of NMR spectra are given in parts per million (ppm). Low and high-resolution matrix-assisted-laserdesorption/ionization (MALDI) mass spectra (MS) were obtained on Bruker Daltonics ultraflex using dithranol acid as a matrix. All steady state absorption spectra were recorded on a JASCO V-570 UV-Vis spectrophotometer. Fluorescence spectra were measured on fluorescence spectrophotometer (F-2700, Hitachi High-Technologies). Relative quantum vield measurements were performed using FP-6500 spectrofluorometer (JASCO). Absolute quantum vields in solid state were measured on FP-6500 spectrofluorometer with an ISF-513 fluorescence integrate sphere unit (JASCO). Emission lifetimes were estimated upon excitation at 355 nm by picosecond pulse train (~7 ps pulse width, 1 kHz repetition) from a Nd:YVO₄ laser (PL2250, EKSPLA, \sim 12 mW). Emission was corrected and guided into a monochromator (C5094, Hamamatsu), then picked by a streak scope (C4334, Hamamatsu) equipped with micro-channel plate (MCP). Slit width of monochromator was adjusted to 200 µm corresponding to the wavelength resolution of 12 nm. Emission kinetic traces were averaged over 20 nm wavelength range around their peak tops (520–540 nm). The single crystals were obtained by slow evaporation of a mixed solution (CH₂Cl₂/Hexane) for Ia and data collections were performed on a Rigaku R-AXIS-RAPID diffractometer with Cu-K α radiation ($\lambda = 0.7107$ Å) at -130°C. DSC measurements were performed on a PerkinElmer model DSC 8000 differential scanning calorimeter. Powder XRD measurements were performed on MiniFlex 600, Rigaku make in the range of $2\theta = 2-30^{\circ}$. All theoretical calculations were performed using Gaussian 09 package (Similar characterization techniques were used for reported positional isomers¹ Ib and IIb). X-ray diffraction measurements were carried out using a synchrotron radiation X-ray beam with a wavelength of 0.108 nm on BL44B2 at the Super Photon Ring (SPring-8, Hyogo, Japan). A large Debye–Scherrer camera was used in conjunction with an imaging plate as a detector, and all diffraction patterns were recorded with a 0.01° step in 2θ . During the measurements, samples were put into a 0.5-mm thick glass capillary and rotated to obtain a homogeneous diffraction pattern. The exposure time to the X-ray beam was 1.5 min. The temperature was controlled by high-temperature N2 gas flow. Heating and cooling process was carried out at a rate of 10° C min⁻¹ and annealed at the target temperature for 2 min prior to the beam exposure.

Synthetic Details

Scheme S1. Synthesis of Ia and IIa.



a: n-BuLi/THF, -78 $^{o}\text{C};$ b: B(OMe)_3; c: Propane-1,3-diol, toluene, reflux

d: PCI₃, toluene, reflux; e: Pd(PPh₃)₄, K_2CO_3 , toluene, water, reflux

Scheme S2. Synthesis of IIa0 and IIa1.



a: NaH / CH₃I / DMF/ R.T; b: Pd(PPh₃)₄, K₂CO₃ / H₂O, toluene, reflux c: 1. eq BBr₃ / DCM at - 78 $^{\circ}$ C, R.T, 48 h

Synthesis of 2a and 2b



9,9-Dihexylfluorene-2,7-bis(trimethylene boronates) (2a)

Intermediate **2a** was prepared according to literature procedure.³⁶ *n*-BuLi (1.6 M in hexane, 3.8 mL, 6.0 mmol) was added dropwise into a solution of 2,7-dibromo-9,9-dihexylfluorene **1a** (1 g, 2.0 mmol) in anhydrous THF (30 mL) at -78° C. The reaction was stirred for 3 h prior to the addition of methyl borate (2.3 mL, 20 mmol) in one portion. The mixture was stirred at -78° C for 1h after addition of trimethyl borate and warmed to room temperature and stirred for 22 h. The reaction mass was poured into crushed ice containing 2M HCl (70 mL) with constant stirring. The reaction mixture was extracted with diethyl ether (60 mL × 2) and the combined extracts were evaporated to give yellow colored solid, boronic acid as intermediate. This intermediate was refluxed with 1,3-propanediol (0.40 mL, 4.9 mmol) in 40 mL toluene for 12 h. The reaction mass was concentrated under vacuum and the obtained solid was purified by column chromatography (with silica gel and *n*-hexane/ethyl acetate as eluent) to obtain a yellow colored solid **2a** (Yield after column chromatography: 0.65 g, 64%).

¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 7.73–7.66 (m, 6H), 4.20–4.18 (t, 8H), 2.09–2.06 (m, 4H), 1.99–1.95 (m, 4H), 1.15–0.97 (m, 12H), 0.74–0.70 (m, 6H), 0.70–0.50 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ ppm 150.3, 143.6, 132.5, 127.9, 127.6, 119.2, 62.1, 54.9, 40.6, 40.4, 31.6, 29.8, 27.5, 23.7, 22.7, 14.1.

MALDI-TOF (*m*/*z*): calcd 502.34, found 503.11.

9,9-Dioctylfluorene-2,7-bis(trimethylene boronates) (2b)

Intermediate **2b** was prepared by slight modification of reported procedure.^{SII} *n*-BuLi (1.6 M in hexane, 3.4 mL, 5.5 mmol) was added dropwise into a solution of 2,7-dibromo-9,9-octylfluorene **1b** (1 g, 1.8 mmol) in anhydrous THF (30 mL) at -78° C. The reaction was stirred for 2.5 h prior to the addition of methyl borate (2.0 mL, 18 mmol) in one portion. The mixture was stirred at -78° C for 1h after addition of tri-methyl borate and warmed to room temperature and stirred for 24 h. The reaction mass was poured into crushed ice containing 2 M HCl (70 mL) with constant stirring. The reaction mixture was extracted with diethyl ether (60 mL × 2) and the combined extracts were evaporated to give yellow colored solid as a boronic acid intermediate. This obtained intermediate was further refluxed with 1,3-propanediol (0.32 mL, 4.4 mmol) in 40 mL toluene for 12 h. The reaction mass was concentrated under vacuum and the obtained liquid was purified by column chromatography (with silica gel and *n*-hexane/ethyl acetate as the eluent) to obtain a yellow liquid **2b** (Yield after column chromatography: 0.82 g, 81%).

¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 7.74–7.66 (m, 6H), 4.20–4.17 (t, 8H), 2.08–2.06 (m, 4H), 1.98–1.94 (m, 4H), 1.27– 0.98 (m, 20 H), 0.84–0.52 (m, 10H).

¹³C NMR (100 MHz, CDCl₃): *δ* ppm 150.3, 143.6, 132.3, 127.9, 119.2, 62.1, 54.9, 40.4, 31.8, 30.1, 29.4, 29.3, 22.6, 14.1. MALDI–TOF (*m*/*z*): calcd 558.41, found 558.76.

Synthesis of 5



2-(Benzo[d]thiazole-2-yl)-5-bromophenol (5)

Phosphorus trichloride (0.63 g, 4.6 mmol) was added dropwise to a solution of 4-bromo-2-hydroxybenzoic acid 4 (1.0 g, 4.6 mmol) and 2-aminothiophenol **3** (0.69 g, 5.5 mmol) in toluene (40 mL), maintaining the temperature below 40°C. The mixture was refluxed for 8 h, after completion of reaction monitored by TLC; reaction mixture was neutralized with aqueous sodium carbonate solution (20% w/v). Toluene was removed by vacuum distillation and crude product was extracted from chloroform which was further purified by column chromatography on silica gel (hexane/ethyl acetate: 90/10 v/v) to yield 2-(benzo[*d*]thiazole-2-yl)-5-bromophenol **5** as white solid (Yield after column chromatography: 0.7 g, 50%).

¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 12.70 (s, 1H), 7.97–7.99 (dd, 1H), 7.89–7.91 (dd, 1H), 7.49–7.54 (m, 2H), 7.40–7.44 (m, 1H), 7.29 (d, 1H), 7.10–7.07 (dd, 1H).

MALDI–TOF (*m*/*z*): calcd 304.95, found 305.92.

Synthesis of 6



2-(4-Bromo-2-methoxyphenyl)benzo[d]thiazole (6)

2-(4-Bromo-2-methoxyphenyl)benzo[d]thiazole 6 was prepared from 2-(benzo[d]thiazole-2-yl)-5-bromophenol 5 by methylation reaction. Intermediate 5 (0.5 g, 1.6 mmol) was reacted with methyl iodide (0.34 g, 2.4 mmol) in presence of sodium hydride (0.045 g, 1.9 mmol) in DMF (20 mL) for 1h. After completion of reaction, reaction mixture was quenched in 100 g crushed ice. White color product was separated that was further isolated by filtration and purified by column chromatography. Yield after chromatography: 0.4 g, 76%, white solid.

¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 8.39–8.41 (d, 1H), 8.06–8.08 (d, 1H), 7.91–7.93 (d, 1H), 7.42–7.51 (t, 1H), 7.35–7.39 (t, 1H), 7.28 (dd, 2H), 7.21 (d, 1H), 4.06 (s, 1H).

MALDI-TOF (m/z): calcd 318.97, found 319.91.

Synthesis of Ia and IIa



5,5'-(9,9-Dihexyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) (Ia)

9,9-Dihexylfluorene-2,7-bis-trimethylene boronate **2a** (0.5 g, 0.99 mmol), 2-(Benzo[*d*]thiazole-2-yl)-5-bromophenol **5** (0.66 g, 2.19 mmol) and Pd(PPh₃)₄ (0.11 g, 0.099 mmol) were added to a mixture of 20 mL degassed toluene (three times) and aqueous (degassed water 7 mL) 2 M K₂CO₃ under nitrogen atmosphere. The mixture was stirred at 110°C for 24 h. After completion of reaction (monitored by TLC), the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with chloroform. The combined organic layers were washed with water and dried over sodium sulfate. A white colored solid was obtained after the concentration of organic layers. The crude product was purified by column chromatography (with silica gel and ethyl acetate/hexane as eluent). Yield after column chromatography: 0.39 g, 42%. ¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 12.64 (s, 2H), 8.02–8.04 (d, 2H), 7.92–7.94 (d, 2H), 7.78–7.82 (t, 4H), 7.65–7.69 (t, 4H), 7.51–7.55 (t, 2H), 7.41–7.45(t, 4H), 7.30–7.32 (dd, 2H), 2.05–2.09 (m, 4H), 1.05–1.15 (m, 12 H), 0.74–0.78 (m, 10H). ¹³C NMR (100 MHz, CDCl₃, 20°C): δ ppm 169.0, 158.1, 151.9, 145.9, 140.8, 138.8, 132.5, 128.8, 126.7, 126.1, 125.5, 122.1, 121.5, 121.4, 120.2, 118.5, 115.9, 115.6, 55.4, 40.4, 31.4, 29.7, 23.8, 22.6, 14.0. APCI–HRMS (*m/z*): calcd for [M + H]⁺ 785.3230, found 785.3213.

5,5'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) (IIa)

9,9-Dioctylfluorene-2,7-bis-trimethylene boronate **2b** (0.2 g, 0.35 mmol), 2-(benzo[*d*]thiazole-2-yl)-5-bromophenol **5** (0.24 g, 0.78 mmol) and Pd(PPh₃)₄ (0.041 g, 0.035 mmol) were added to a mixture of 20 mL degassed toluene (three times) and aqueous (degassed water 6 mL) 2 M K₂CO₃ under nitrogen atmosphere. The mixture was stirred at 120°C for 24 h. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with chloroform. The combined organic layers were washed with water and dried over sodium sulfate. A white colored solid was obtained after the concentration of organic layers. The crude product was purified by column chromatography (with silica gel and ethyl acetate/hexane as eluent). Yield after column chromatography: 0.12 g, 40%. ¹H NMR (400 MHz, CDCl₃, 20°C): δ ppm 12.63 (s, 2H), 8.02–8.04 (d, 2H), 7.92–7.94 (d, 2H), 7.78–7.83 (t, 4H), 7.65–7.69 (t, 4H), 7.51–7.55 (t, 2H), 7.41–7.45(t, 4H), 7.30–7.32 (dd, 2H), 2.05–2.09 (m, 4H), 1.08–1.19 (m, 20 H), 0.73–0.81 (m, 10H). ¹³C NMR (100 MHz, CDCl₃, 20°C): δ ppm 169.2, 158.3, 151.9, 146.0, 140.8, 138.7, 132.7, 128.7, 126.7, 126.0, 125.6, 122.2, 121.5, 121.4, 120.4, 118.6, 116.0, 115.6, 55.2, 40.4, 31.7, 30.0, 29.1, 28.9, 23.7, 22.4, 14.1. APCI–HRMS (*m/z*): calcd for [M + H]⁺ 841.3856, found 841.3832.

Synthesis of IIa0 and IIa1



2,2'((9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(2-methoxy-4,1-phenylene))bis(benzo[d]thiazole) (IIa0)

(9,9-Dioctyl-9H-fluorene-2,7-diyl)diboronic acid 7 (0.29 g, 0.60 mmol), 2-(4-bromo-2-methoxyphenyl)benzo[*d*] thiazole 6 (0.40 g, 1.2 mmol) and Pd(PPh_3)_4 (0.014 g, 0.012 mmol) were added to a mixture of 20 mL degassed toluene (three times) and aqueous (degassed water 10 mL) 2 M K_2CO_3 under nitrogen atmosphere. The mixture was stirred at 110°C for 24 h. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with chloroform. The combined organic layers were washed with water and dried over sodium sulfate. A white colored solid was obtained after the concentration of organic layers. The crude product **Ha0** was purified by column chromatography (with silica gel and ethyl acetate/hexane as eluent: 5/95 v/v) followed by HPLC (eluent: chloroform; 7.5 mL min⁻¹) to allow isolation of **Ha0** as buff-white colored solid. Yield after column chromatography: 0.4 g, 74%.

¹H NMR (400 MHz, CDCl₃, 20°C): *δ* ppm 8.63–8.65 (d, 2H), 8.10–8.13 (d, 2H), 7.94–7.96 (d, 2H), 7.83–7.84 (d, 2H), 7.64–7.68 (m, 4H), 7.49–7.53 (m, 2H), 7.44–7.46 (dd, 2H), 7.34–7.40 (m, 4H), 4.19 (s, 6H), 2.08–2.12 (m, 4H), 1.10–1.19 (m, 20H), 0.77–0.80 (m, 10H).

¹³C NMR (100 MHz, CDCl₃, 20°C): δ ppm 162.91, 157.56, 152.25, 151.96, 145.24, 140.66, 139.39, 136.11, 129.87, 126.26, 125.95, 124.57, 122.73, 121.53, 121.21, 120.28, 120.14, 110.37, 55.85, 55.47, 53.43, 40.31, 31.76, 29.90, 29.13, 24.08, 22.61, 14.35

APCI-HRMS (m/z): calcd for $[M + H]^+$ 869.4169, found 869.4147.

2(Benzo[d]thiazol-2-yl)-5-(7-(4-(benzo[d]thiazole-2-yl)-3-methoxyphenyl)-9,9-dioctyl-9H-fluorene-2-yl)phenol (IIa1)

Compound **Ha1** was prepared by demethylation reaction of compound **Ha0**. BBr₃ (0.03 g, 0.12 mmol) was added dropwise to compound **Ha0** (0.10 g, 0.11 mmol) that was dissolved in dichloromethane (20 mL) at -78° C under N₂ atm. After addition of BBr₃ reaction mixture was stirred for 48 h at room temperature. After 48 h, reaction mixture was quenched in ice water and product was extracted twice with dichloromethane (20 mL × 3). The combined organic layers were washed with water and dried over sodium sulfate. A yellow colored solid was obtained after the concentration of organic layers as crude product. The obtained crude product was mixture of monohydroxy **Ha1** and dihydroxy compounds **Ha**. The desired product **Ha1** was separated by column chromatography (with silica gel and ethyl acetate/hexane as eluent: 3/97 v/v) and further purified by HPLC (eluent: chloroform, 7.5 mL min⁻¹) to allow isolation of **Ha1**. Yield after column chromatography: 0.03 g, 30%, green-yellow crystal (**Ha1**) and yellow solid compound (**Ha**) 0.025 g, 25%.

¹H NMR (**Ha1**: 400 MHz, CDCl₃, 20°C): *δ* ppm 12.62 (s, 1H), 8.62–8.64 (d, 1H), 8.11–8.13 (d, 1H), 8.02–8.04(d, 1H), 7.92–7.96 (t, 2H), 7.78–7.83 (m, 3H), 7.63–7.69 (m, 4H), 7.49–7.55 (m, 2H), 7.43–7.46 (m, 3H), 7.36–7.41 (m, 1H), 7.30–7.35(m, 2H), 4.19 (s, 3H), 2.06–2.10 (m, 4H), 1.09–1.19 (m, 20H), 0.72–0.80 (m 10H).

¹³C NMR (**Ha1**: 100 MHz, CDCl₃, 20°C): *δ* ppm 169.04, 162.93, 158.19, 157.56, 152.25, 152.01, 151.95, 151.88, 145.95, 145.25, 140.76, 140.70, 139.37, 138.86, 136.11, 132.60, 129.86, 128.82, 126.75, 126.24, 126.12, 125.94, 125.53, 124.56, 122.72, 122.14, 121.53, 121.50, 121.21, 121.18, 120.28, 120.14, 118.56, 115.94, 115.71, 110.37, 55.85, 55.43, 40.36, 31.75, 29.98, 29.19, 23.85, 22.59, 14.06.

APCI-HRMS (m/z): calcd for $[M + H]^+$ 855.3988, found 855.4012.



Figure S1. APCI-HRMS charts for (a) Ia, (b) IIa, (c) IIa0, and (d) IIa1.



Figure S2. Steady state absorption spectra of (a) Ia and (b) IIa in different solvents at room temperature $(10^{-5} \text{ M concentration})$.



Figure S3. Absorption spectra of (a) Ia and (b) IIa under deprotonation reaction in DMF by adding equivalent NaH at room temp (10^{-5} M conc) .



Figure S4. Normalized emission spectra of (a) Ia and (b) IIa in different solvents at room temperature (10^{-5} M concentration), $\lambda_{ex} = 375$ nm.



Figure S5. Decay profiles of emission from solid state (a) Ia and (b) IIa at 530 nm upon excitation at 355 nm as well as (c) the fitting results.



Figure S6. Normalized (a) absorption and (b) emission spectra of compounds Ia in THF and THF/water mixture (room temperature, 10^{-5} M concentration, $\lambda_{ex} = 375$ nm). The % values represent the volume content of water in THF/water mixture.



Figure S7. ¹H NMR spectra of **IIa** in THF- d_8 with the addition of D₂O or TFA. (a) and (b) represent different chemical shift regions.



Figure S8. AFM Images of compound Ia in THF/water mixture. AFM images of spin-coated compound Ia in THF/water mixture at concentration 10^{-5} M with different water fractions (v/v): 40/60, 30/70, 20/80, 10/90, and 5/95. Samples were spin-coated from the solution on HOPG (highly oriented pyrolytic graphite) substrate at 2000 rpm.



Figure S9. (a,c,e) Absorption and (b,d,f) emission spectra of (a,b) Ha0, (c,d) Ha1, and (e,f) Ha in THF and THF/water mixture (room temperature, 10^{-5} M concentration, $\lambda_{ex} = 375$ nm).



Intramolecular rotation (IR); Restriction of intramolecular rotation (RIR)

Figure S10. Intramolecular and restricted intramolecular charge-transfer rotation in non-ESIPT and ESIPT molecules.



Figure S11. Plots of fluorescence quantum efficiency against fraction of water (%) for (a) IIa0 and (b) IIa1 and IIa.



Figure S12. DSC curves for (a) Ia and IIa for two successive cycles, (b) Ib and IIb on first cycle, and (c) Ib and IIb on second cycle.



Figure S13. Powder XRD patterns of Ia and IIa and positional isomer Ib and IIb^{1} .



Figure S14. DSC curves of (a) IIa0 and (b) IIa1 for two successive DSC cycles at the scan rate of 10 °C min⁻¹.



Figure S15. Variable-temperature XRD patterns observed for Ia on heating and cooling.



Figure S16. (a) Crystal structure of Ia with O–N bond length and different torsions, (b) Crystal structure of Ib with O–N bond length and different torsions (c) Crystal structure of Ia side view (d) Crystal structure of Ia along long axis view (e) Crystal structure of Ib side view (f) Crystal structure of Ib along long axis view (CCDC: 1410376 cif file was used for crystal data of Ib¹).



Figure S17. Optimized structures of (a) Ia and (b) Ib.

Comps.	Medium Water: THF	0:100	10:90	20:80	30:70	40:60	50:50	60:40	70:30	80:20	90:10	95:05
Ia	λ_{\max}^{Abs} (nm)	382	382	381	381	381	381	382	436	396	388	388
	λ_{\max}^{Em} (nm)	423 442 518	417 435 513	417 436 513	415 435 512	415 436 513	417 436 513	430 444 513	430 450 513	428 450 515	426 450 513	427 450 514
	$arPhi_{ m f}(\%)$	3.4	5.2	6.3	6.8	7.2	7.9	10.9	33	19	20	22
Ib	λ_{\max}^{Abs} (nm)	334	334	334	334	334	335	335	354	354	344	a
	λ_{\max}^{Em} (nm)	404 553	416 553	417 552	418 552	419 552	418 551	419 550	415 554	554	554	a
	$\Phi_{\rm f}$ (%)	1.5	0.7	2.3	2.4	2.5	2.6	2.7	8.1	7.4	9.1	а

Table S1. AIE data of Ia and Ib.

 $\Phi_{\rm f}$: Fluorescence quantum efficiency, ^a not measured.

Table S2. Optical properties of Ha0 and Ha1 in solid state and solution.

Comps	Medium	λ_{max}^{Abs} (nm)	ε (mol ⁻¹ dm ³ .cm ⁻¹)	λ_{\max}^{Em} (nm)	Stokes shift (nm)	Stokes shift (cm ⁻¹)	Quantum efficiency Φ (%)	Emission Lifetime (ns)
ПаО	^a Solid Film	370	е	429, 452	59, 82	3717, 4903	° 37	0.85
	^b Chloroform	369	122400	417, 439	48, 70	3119, 4321	^d 84	
	^b Toluene	369	122500	414, 436	45, 67	2945, 4165	^d 80	
	^b DMF	379	130680	421, 444	42, 65	2632, 3862	^d 90	
	^b Methanol	372	82700	419, 430	47, 58	3015, 3625	f	
	^b Acetonitrile	373	49000	417, 436	44, 63	2828, 3873	f	
IIal	^a Solid Film	375	е	455, 476, 543	80, 101, 168	4688, 5658, 8250	° 25	0.63
	^b Chloroform	377	117680	420, 509	43, 132	2715, 6878	^d 13	
	^b Toluene	377	115417	417, 439, 516	40, 62, 139	2544, 3746, 7145	^d 14	
	^b DMF	379	108260	419, 441	40, 62	2518, 3709	^d 14	
	^b Methanol	375	90620	418, 440	43, 65	2743, 3939	f	
	^b Acetonitrile	377	128500	417, 510	40, 133	2544, 6917	f	

^a Measured on thin film, spin-cast from (1 wt %) dichloromethane solution. ^b Measured from 10^{-5} M solution. ^c Absolute quantum yields in solid state. ^d Quantum yields measured by relative methods using quinine sulphate standard (10^{-5} M concentration). ^e Not calculated. ^f Not measured.

Table S3. Single crystal data of Ia and Ib.

Comps.	Ia	Ib	
Chemical Formula	$C_{51}H_{48}N_2O_2S_2$	$C_{51}H_{48}\overline{N_2O_2S_2}$	
Formula Mass	785.07	785.07	
Temperature [°C]	-130	-150	
λ[Å]	0.7107	1.54187	
Crystal system	triclinic	triclinic	
Space group	P -1 (#2)	P -1 (#2)	
Ζ	2	2	
<i>a</i> [Å]	10.590(2)	11.7603(2)	
<i>b</i> [Å]	11.981(3)	14.1138(3)	
<i>c</i> [Å]	18.082(4)	14.5223(3)	
α[deg]	101.0628(12)	65.8221(8)	
β[deg]	101.771(3)	86.8240(9)	
γ[deg]	107.130(3)	70.2805(8)	
Unit cell volume $[Å^3]$	2067.2(8)	2060.39(7)	
$\rho_{\text{calcd}} [\text{g cm}^{-3}]$	1.261	1.265	
Collected data	16953	23668	
Unique data / <i>R</i> _{int}	9112/0.0289	7367/ 0.0477	
No. of parameters	514	522	
Goodness-of-fit ^[a]	1.514	1.085	
<i>R</i> 1 ($I > 2\sigma$), <i>wR</i> 2 (all reflections) ^[b]	0.1188,	0.0418,	
· · · · ·	0.3942	0.1171	
Residual density [e Å ⁻³]	3.17/-1.09	0.29/-0.46	

Table S4. Structural parameters of Ia and Ib of enol forms in ground and S1 states.

Comme	D = u d 1 = u = 4h /= u = 1 = =	Electro	0.0		
Comps.	Bond length/angles	\mathbf{S}_{0}	\mathbf{S}_1	51-50	
	O ₂₇ -H ₅₆	0.992	0.994	0.002	
	N ₇₂ -H ₅₆	1.736	1.721	0.015	
	$C_{20}-C_{18}$	1.452	1.434	0.018	
	C ₂₀ -N ₇₂	1.310	1.324	0.024	
Ia	O ₂₇ -H ₅₆ -N ₇₂	147	148	1	
	O ₄₁ -H ₆₃	0.992	0.994	0.002	
	N ₇₃ -H ₆₃	1.735	1.720	0.015	
	$C_{31}-C_{32}$	1.424	1.438	0.014	
	C ₃₄ -73	1.310	1.325	0.015	
	O ₄₁ -H ₆₃ -N ₇₃	147	148	1	
	O ₂₇ -H ₅₇	0.992	1.022	0.030	
	N ₇₄ -H ₅₇	1.733	1.611	0.122	
	$C_{20}-C_{18}$	1.455	1.432	0.023	
	C ₂₀ -N ₇₄	1.310	1.351	0.041	
ањ	O ₂₇ -H ₅₇ -N ₇₄	147	151	4	
10	O ₄₁ -H ₆₅	0.992	0.998	0.006	
	N ₇₅ -H ₆₅	1.733	1.706	0.027	
	$C_{32}-C_{34}$	1.455	1.458	0.003	
	C ₃₄ -N ₇₅	1.310	1.309	0.001	
	O ₄₁ -H ₆₅ -N ₇₅	147	147	0	

Bond lengths in Å, bond angles in °, ^a Previously reported data¹

X-ray single crystal data of compound Ia and Ib.

The single crystal of **Ia** (CCDC 1449566) was obtained by the slow evaporation of a mixed solution (dichloromethane and hexane). Data collections were performed on a Rigaku Saturn70 CCD diffractometer with Mo-K α radiation ($\lambda = 0.71075$ Å) at -130° C. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms except for OH groups were restrained to ride on the atom to which they are bonded. All the calculations were performed by using Crystal Structure crystallographic software package, ^{S12} except for refinement, which was performed by using SHELXL-97. ^{S13}

Crystallographic data of **Ib** was described in our previous report.^{S11}

Calculation of Goodness-of-fit^[a], R_1 (I > 2 σ), w R_2 (all reflections)^[b]

[a] GOF = $\left\{ \left[w \left(F_0^2 - F_c^2 \right)^2 \right] / (n-p) \right\}^2$, where *n* and *p* denote the number of data and parameters.

[b] R1 = $\sum (\|F_0\| - \|F_c\|) / \sum \|F_0\|$ and wR2 = $\left\{ \sum \left[w (F_0^2 - F_c^2)^2 \right] / \sum \left[w (F_0^2)^2 \right] \right\}^2$ where $w = 1 / \left[\sigma^2 (F_0^2) + (a \cdot P)^2 + b \cdot P \right]$ and $P = \left[(Max; 0, F_0^2) + 2 \cdot F_c^2 \right] / 3.$

Supporting References

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- 3. Sheldrick, G. M. Acta Cryst. A 2008, 64, 112–122.