

Supporting Information

**Aggregation-induced emission active D- π -A binaphthyl
luminophore with dual-mode fluorescence**

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Experimental Section

S1. Instrumental

All the ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz JEOL LMN-EX400 instrument and 300 MHz BRUKER DPX300 with tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a JASCO FT-IR 469 plus spectrometer. Melting points were obtained by polarized optical microscopy (POM) (Leica DM2500P microscopy with a Mettler FP90 hot stage). MS spectra (EI+) were obtained by JEOL JMS700 mass spectrometer. Except for measurement of aggregation induced emission in DMF- water system, all photophysical measurements performed in solutions were carried out using dilute solutions with optical density (O.D.) around 0.1 at the maximum absorption wavelength in 1 cm path length quartz cells at room temperature (298 K). In the measurement of aggregation induced emission in DMF-water system, solute concentration was fixed to 1.78×10^{-5} M regardless of volume fraction of water. In addition, all samples solutions were deaerated by bubbling with argon gas for 15 min before the measurements. UV-Vis spectra were recorded with a JASCO V-670 UV-Vis Spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 Spectrofluorometer. Absolute quantum yields were measured by a Hamamatsu Photonics Quantaaurus QY. Fluorescence lifetimes were measured at the most intense peaks using a Hamamatsu Photonics OB 920 Fluorescence Lifetime Spectrometer equipped with LEDs lamp (343 nm).

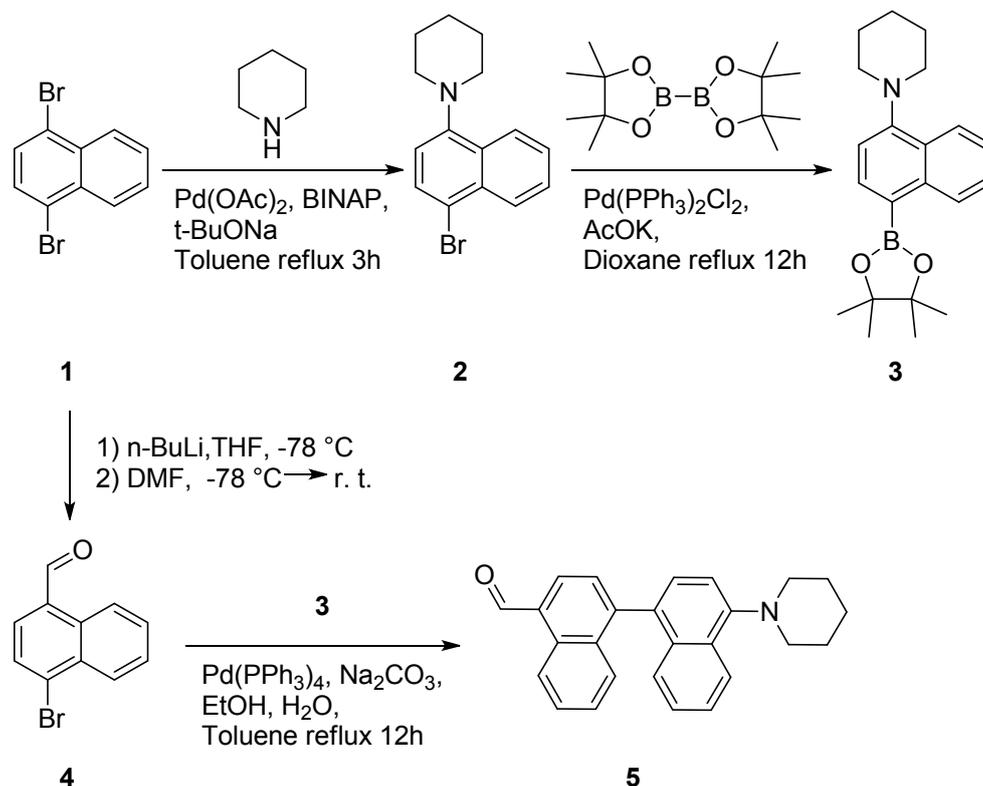
S2. Materials

Unless otherwise noted, all reagents and chemicals were used without further purification. 1,4-dibromonaphthalene, (\pm)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, sodium *tert*-butoxide, tetrakis(triphenylphosphine)palladium(0), and bis(pinacolato)diboron were obtained from TCI (Tokyo, Japan). bis(triphenylphosphine)palladium(II) dichloride, and anhydrous DMF were purchased from Sigma-Aldrich Japan 3 (Tokyo, Japan). Ethanol, dioxane, potassium acetate and piperidine was purchased from Wako Pure Chem (Tokyo, Japan). *n*-Buthyllithium, spectrograde ethyl acetate, acetonitrile and anhydrous THF were obtained from Kanto Chem. (Tokyo, Japan). Spectrograde hexane, isopentane, toluene, diethyl ether, THF, chloroform, dichloromethane, DMF, ethanol, methanol, magnesium sulphate, sodium

carbonate, sodium hydroxide and 4Å molecular sieve were purchased from Nacalai Tasque (Kyoto, Japan).

S3. Synthesis of 4-formyl-4'-piperidyl-1,1'-binaphthyl (5)

4-formyl-4'-piperidyl-1,1'-binaphthyl (5) was synthesized according to in Scheme S1.



Scheme S1. Synthesis of 5.

4-Bromo-1-piperidinyl-naphthalene (2)

A solution of sodium *tert*-butoxide (0.24 g, 2.5 mmol), palladium acetate (20 mg, 0.088 mmol), 1,4-dibromonaphthalene (0.5 g, 1.8 mmol), and (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (0.16 g, 0.26 mmol) in toluene (10 mL) was stirred for 15 min under argon atmosphere, and the resulting solution was heated to 100 °C. After further stirring for 15 min, piperidine (0.21 mL, 2.1 mmol) was added. The resulting mixture was stirred at 100 °C for 3 h. The reaction was quenched by the addition of water; then, the mixture was filtered and its filtrate was extracted with ethyl acetate. The organic layer was washed with water and brine and then dried over MgSO₄. The solvent was removed in *vacuo*, and the residue was purified by column

chromatography on silica gel (hexane:chloroform = 5:2) to give crude **2** (387 mg) as yellow-brown viscous liquid. The obtained **2** was used for the next reaction without further purification. Yield : 76%; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.23-8.19 (m, 2H), 7.66 (d, $^3J = 8.0$ Hz, 1H), 7.58-7.51 (m, 2H), 6.91 (d, $^3J = 8.0$ Hz, 1H), 3.01 (broad s, 4H), 1.85-1.82 (m, 4H), 1.67 (broad s, 2H) ppm.

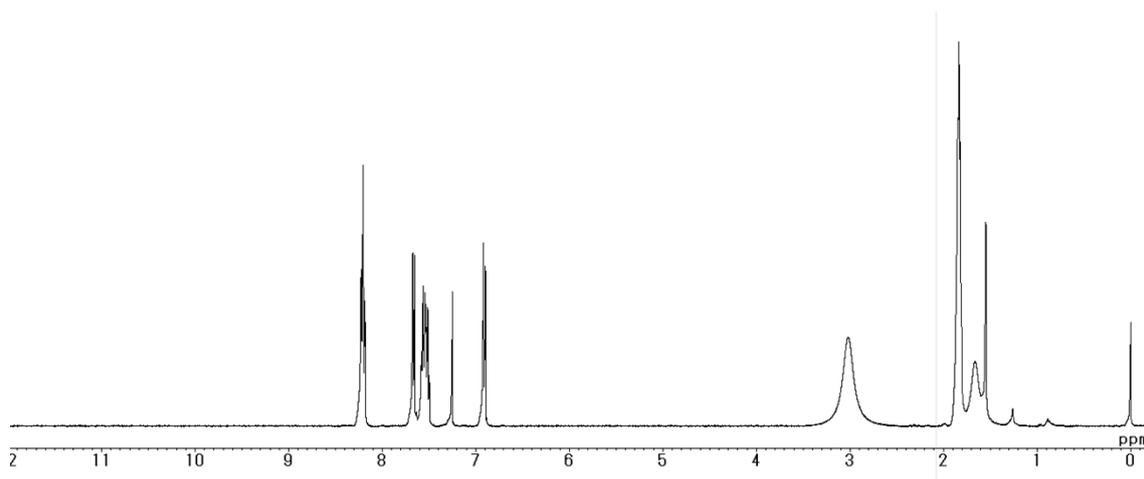


Figure S1. $^1\text{H NMR}$ spectrum of **2**.

4-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolanyl)-1-piperizylnaphthalene (3)

20 ml of 1,4-dioxane was deaerated through argon bubbling and subsequently added to a mixture of **2** (0.62 g, 2.15 mmol), bis(pinacolato)diboron (0.66 g, 2.58 mmol), potassium acetate (0.51 g, 5.17 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.075 g, 0.11 mmol) under argon atmosphere. After the reaction mixture was stirred for 15 min at room temperature, the temperature was raised to 100 °C. The reaction mixture was stirred for 24 h keeping the same temperature. The reaction mixture was quenched by addition of water and then extracted with ethyl acetate, and washed with water and brine. Then, the combined organic layer was dried over MgSO_4 . The solvent was removed in *vacuo*, and the residue was purified by column chromatography on silica gel (Hexane:chloroform = 5:2, then Hexane:ethyl acetate = 10:1) to give crude **3** (0.49 g) as a yellow solid. The crude product of **3** was used for the next reaction without further purification. Yield : 68%; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.76 (dd, $^3J = 7.5$ Hz, $^4J = 0.9$ Hz, 1H), 8.19-8.17 (m, 1H), 8.01 (d, $^3J = 7.5$ Hz, 1H), 7.51-7.42 (m, 2H), 7.02 (d, $^3J = 7.6$ Hz, 1H), 3.06 (broad s, 4H), 1.85-1.81 (m, 4H), 1.66 (broad s, 2H), 1.40 (s, 12H) ppm.

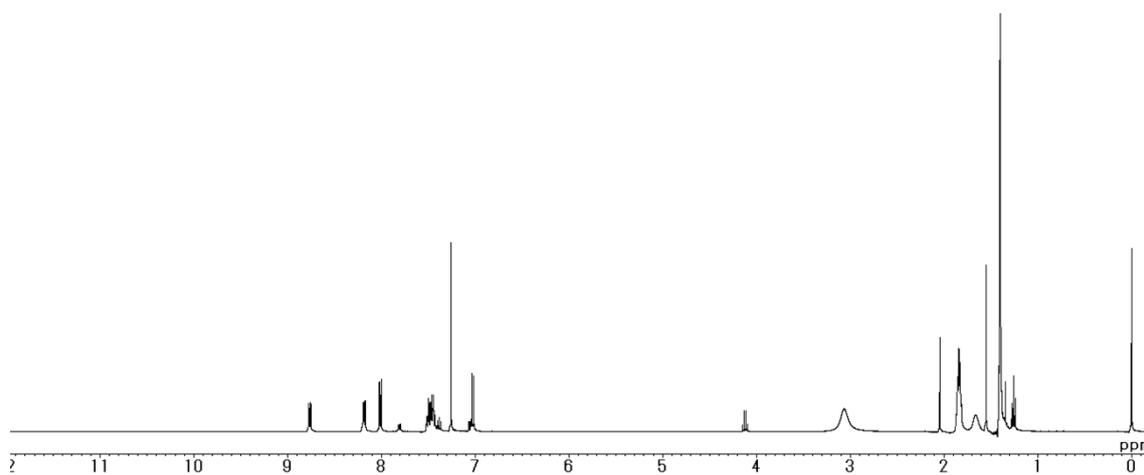


Figure S2. ^1H NMR spectrum of **3**.

4-Bromo-1-naphthaldehyde (4)

Whole reaction apparatus underwent flame dry in *vacuo* before any reaction procedure was conducted. A 2.6 M solution of *n*-butyllithium in hexane (1.6 mL, 4.20 mmol) was added dropwise to a solution of 1,4-dibromonaphthalene (1.0 g, 3.50 mmol) in anhydrous THF (20 mL) under argon atmosphere at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred for 30 min at the same temperature, and anhydrous DMF (0.32 mL, 4.20 mmol) was added dropwise to the solution. The resulting mixture was stirred at room temperature for 3 h. The reaction was quenched by adding water; subsequently, the reaction mixture was extracted with ethyl acetate, and washed with water and brine. Then, the combined organic layer was dried over MgSO_4 . The solvent was removed in *vacuo*, and the residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 5:1) to afford crude **4** (0.71 g) as a colorless solid. Yield: 87%; ^1H NMR (400 MHz, CDCl_3): δ 10.38 (s, 1H), 9.29 (dd, $^3J = 7.7\text{ Hz}$, $^4J = 1.2\text{ Hz}$, 1H), 8.38-8.36 (m, 1H), 7.98 (d, $^3J = 7.6\text{ Hz}$, 1H), 7.82 (d, $^3J = 7.6\text{ Hz}$, 1H), 7.77-7.69 (m, 2H) ppm.

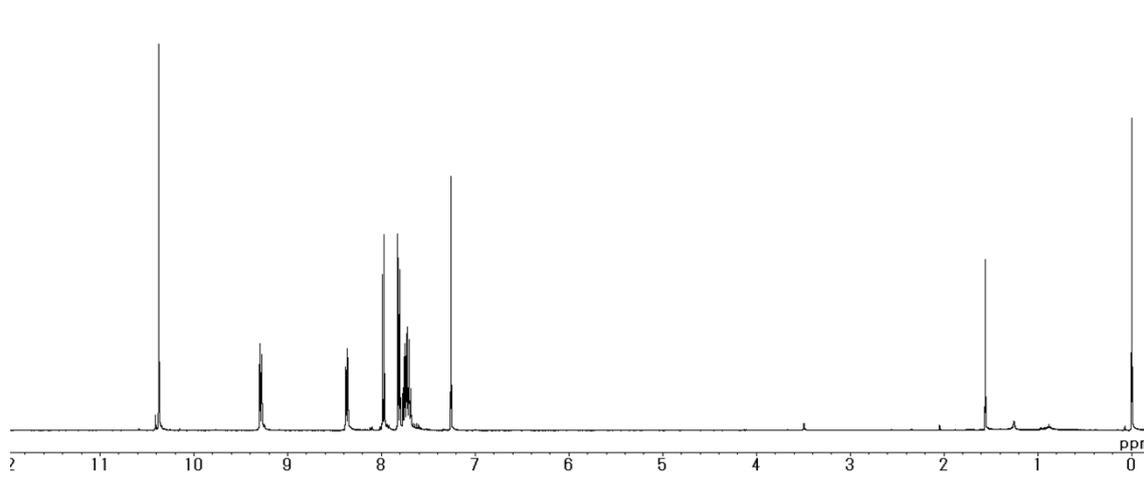


Figure S3. ^1H NMR spectrum of **4**.

4-formyl-4'-piperidyl-1,1'-binaphthyl (5)

A mixture of toluene 15ml, ethanol 6 ml, and water 3ml was deaerated through argon bubbling and subsequently added to a mixture of **3** (0.49 g, 1.46 mmol), 4-bromo-1-naphthaldehyde (**4**) (0.45 g, 1.89 mmol), sodium carbonate (0.46 g, 4.38 mmol), and tetrakis(triphenylphosphine)palladium(0) (85 mg, 0.0073 mmol) under argon atmosphere. After the reaction mixture was stirred for 15 min at room temperature, the temperature of the reaction mixture was raised to 110 °C and stirred for 12 h. The reaction mixture was quenched by cooling to room temperature and then extracted with chloroform, and washed with water and brine. Then, the combined organic layer was dried over MgSO_4 . The solvent was removed in *vacuo*, and the residue was purified by silica gel column chromatography on silica gel (hexane:chloroform = 3:5). After subsequent recrystallisation from hexane, **5** (0.32 g) was obtained as a yellow powder. Yield : 61%; Mp: 184.2-184.8 °C; ^1H NMR (300 MHz, CDCl_3): δ 10.52 (s, 1H, CHO), 9.38 (d, $^3J = 8.6$ Hz, 1H, ArH), 8.36 (d, $^3J = 8.5$ Hz, 1H, ArH), 8.10 (d, $^3J = 7.2$ Hz, 1H, ArH), 7.69 (td, $^3J = 6.9$ Hz, $^4J = 1.4$ Hz, 1H, ArH), 7.67 (d, $^3J = 7.1$ Hz, 1H, ArH), 7.57 (d, $^3J = 8.0$ Hz, 1H, ArH), 7.50 (m, 1H, ArH), 7.40 (td, $^3J = 7.7$ Hz, $^4J = 1.3$ Hz, 1H, ArH), 7.40 (d, $^3J = 7.6$ Hz, 1H, ArH), 7.31-7.29 (m, 1H, ArH), 7.20 (d, $^3J = 7.6$ Hz, 1H, ArH), 3.19 (m, 4H, $-\text{NCH}_2\text{CH}_2-$), 1.94 (quint, $^3J = 5.40$ Hz, 4H, $-\text{NCH}_2\text{CH}_2-$), 1.78-1.71 (m, 2H, $-\text{NCH}_2\text{CH}_2\text{CH}_2-$) ppm.; ^{13}C NMR (75 MHz, CDCl_3): δ 193.5 (CHO), 151.5, 146.7, 136.3, 133.5, 133.4, 132.0, 130.74, 130.70, 128.9, 128.8, 127.6, 127.5, 127.3, 126.8, 126.6, 126.1, 125.2, 124.9, 124.1, 113.9, 54.7 ($-\text{NCH}_2\text{CH}_2-$), 26.6 ($-\text{NCH}_2\text{CH}_2-$), 24.6 ($-\text{NCH}_2\text{CH}_2\text{CH}_2-$) ppm.; FT-IR (KBr): 2921 (C-C stretch on piperizyl group), 2921

(C-C stretch on piperizyl group), 2814 (C-N stretch), 1692 (CHO), 1575 (Ar), 1509 (Ar), 1378 (Ar-N stretch) cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$: C, 85.45; H, 6.34; N, 3.83. Found: C, 85.34; H, 6.36; N, 3.82.

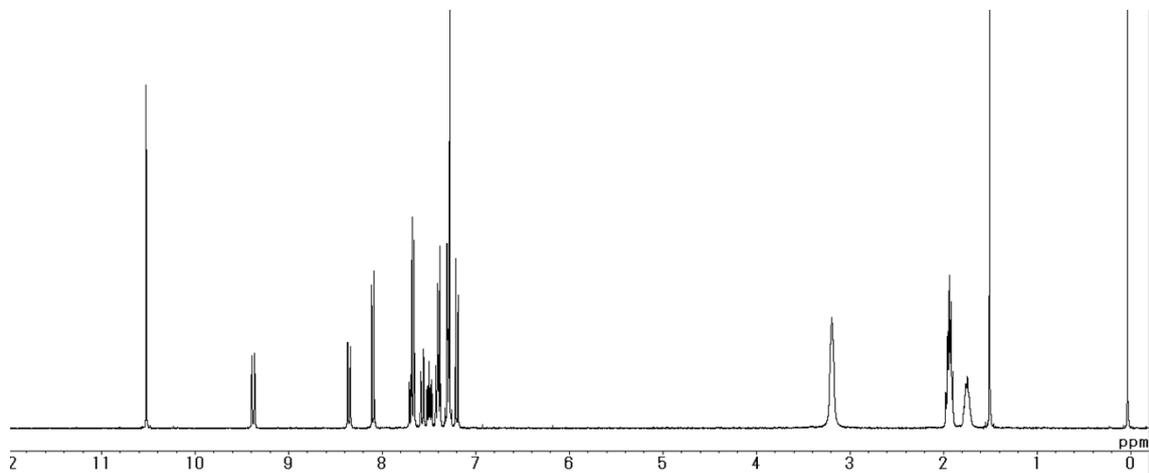


Figure S4. ^1H NMR spectrum of **5**.

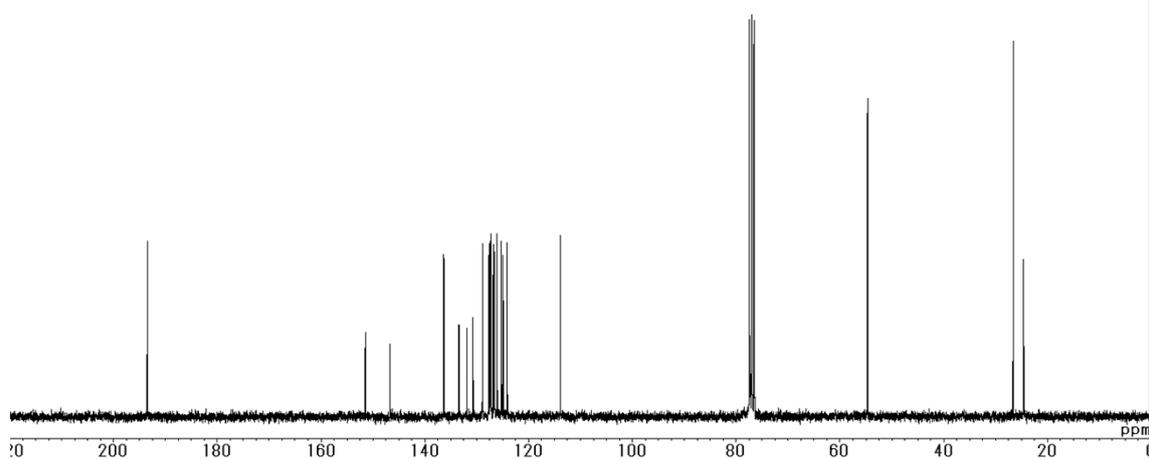


Figure S5. ^{13}C NMR spectrum of **5**.

S4. Photophysical measurement

Table S1. Absorption and fluorescence maxima of **5**.

Solvent	E_T (30)	ϵ [$M^{-1} cm^{-1}$]	λ_{abs} [nm]	λ_{em} [nm]	$\Delta\tilde{\nu}_{St}$ [cm^{-1}]	$\tau_1^{a)}$ [ns]	$\tau_2^{a)}$ [ns]	Φ_F
Hexane	31	15600	330	455	8325	-	-	0.048
Toluene	33.9	15100	332	510	10513	1.19 (0.14)	3.44 (0.86)	0.372
Diethyl ether	34.5	15900	330	522	11146	2.09 (0.09)	4.58 (0.91)	0.338
THF	37.4	15500	330	576	12942	2.45 (0.63)	3.54 (0.37)	0.111
Ethyl acetate	38.1	15800	329	577	13064	-	-	0.062
Dichloromathane	40.7	15500	331	615	13951	-	-	0.041

a) The values in the brackets indicate the relative coefficient of each term of fluorescence lifetime.

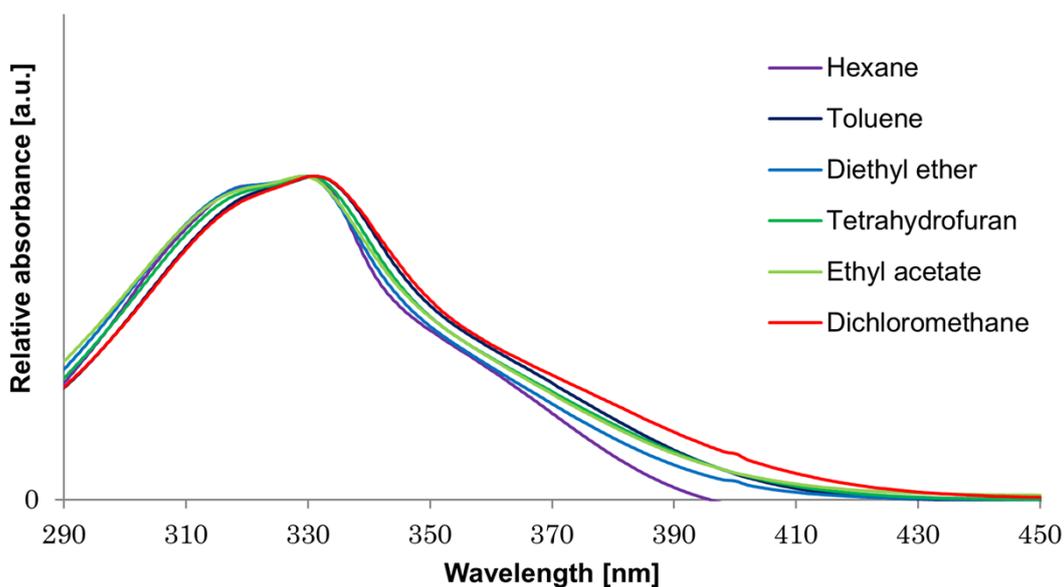


Figure S6. Absorption spectra of **5** in various solvents.

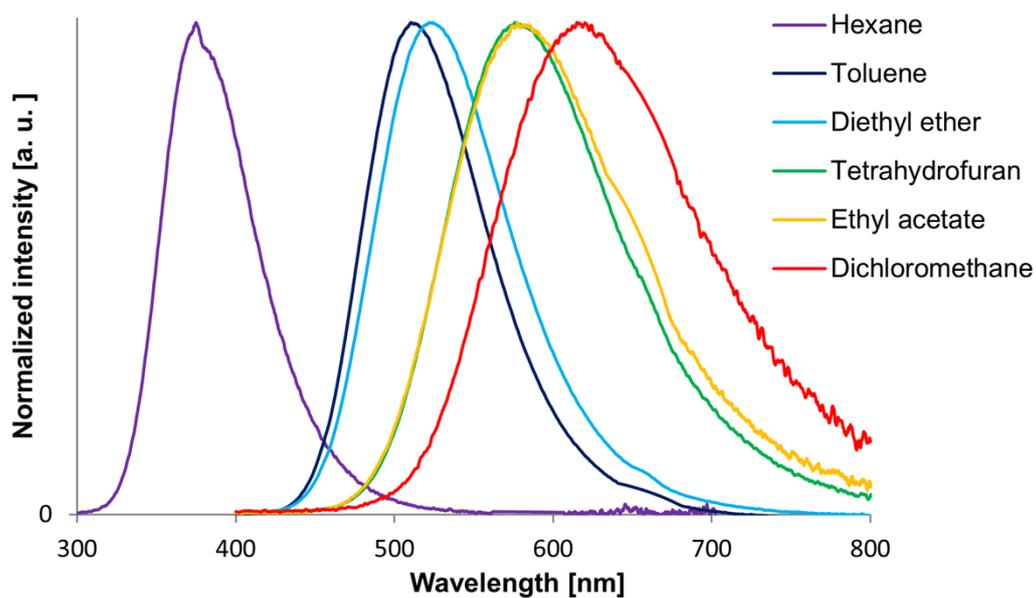


Figure S7. Fluorescence spectra of **5** in various solvents.

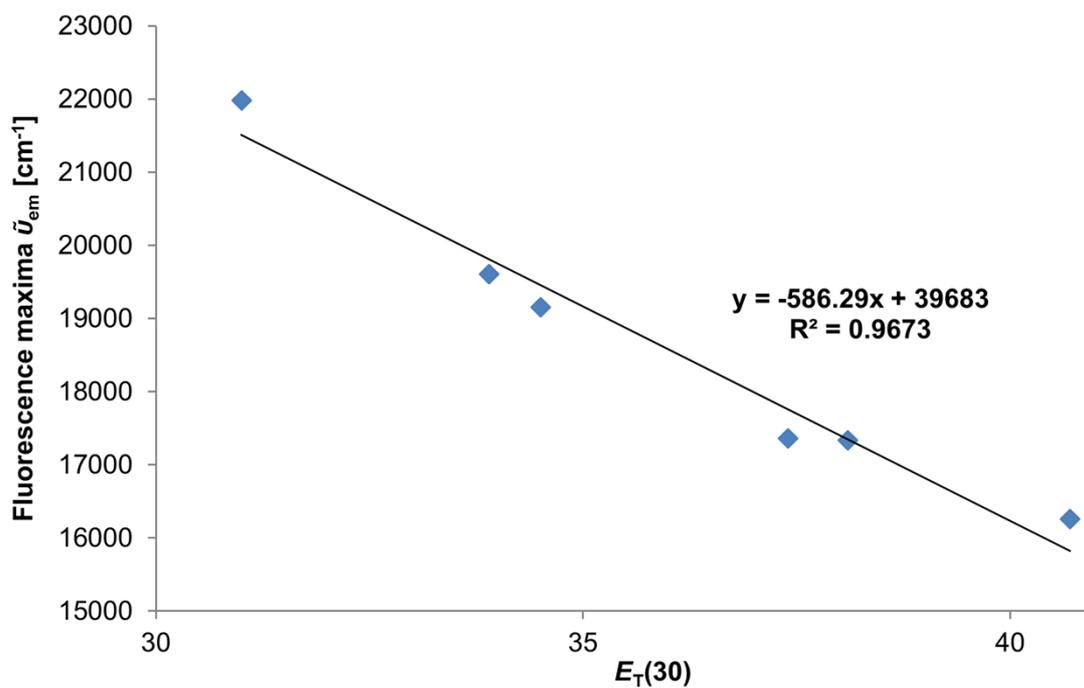


Figure S8. The positions of fluorescence maxima of **5** versus the polarity $E_T(30)$ in aprotic solvents.

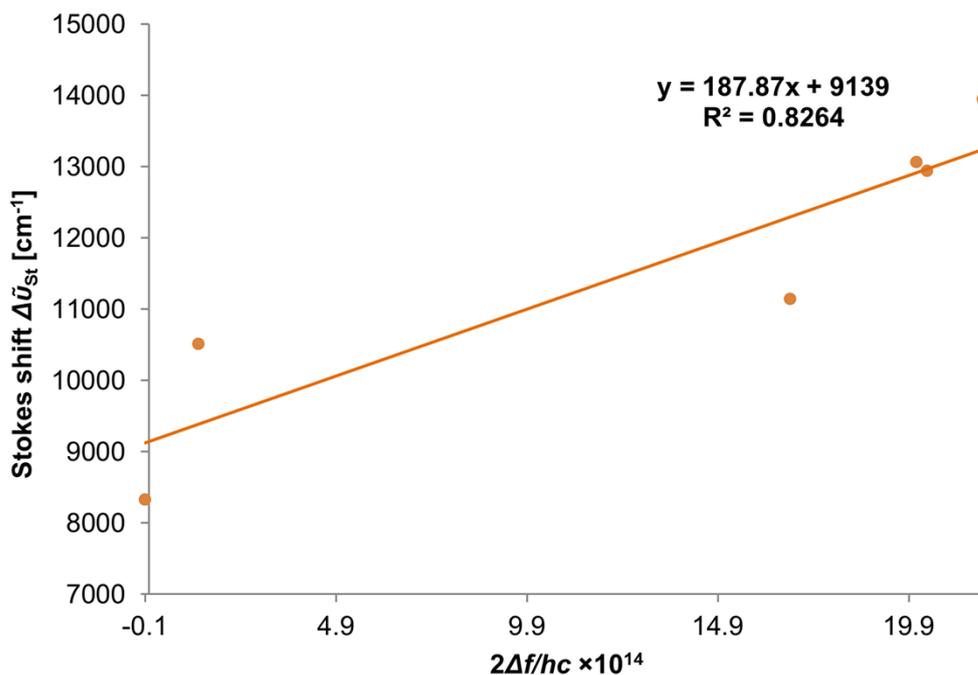


Figure S9. Lippert-Mataga plot of **5**. The transition dipole moments were calculated based on $\Delta\bar{\nu}_{st} = 2\Delta\mu^2\Delta f / hca^3$, $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where c is the speed of light [m/s]; h is Planck's constant [$\text{J} \cdot \text{s}$]; n and ϵ are the refractive index⁵ and dielectric constant⁵, respectively. The data in polar protic solvents were excluded to avoid specific solute-solvent interactions. Following other reports about D- π -A type biphenyl⁶ or 1,1'-binaphthyl⁷ dyes, Onsager cavity radii a was taken as the half-length of the molecular long axis, $a = 5.51 \times 10^{-10}$ [m].

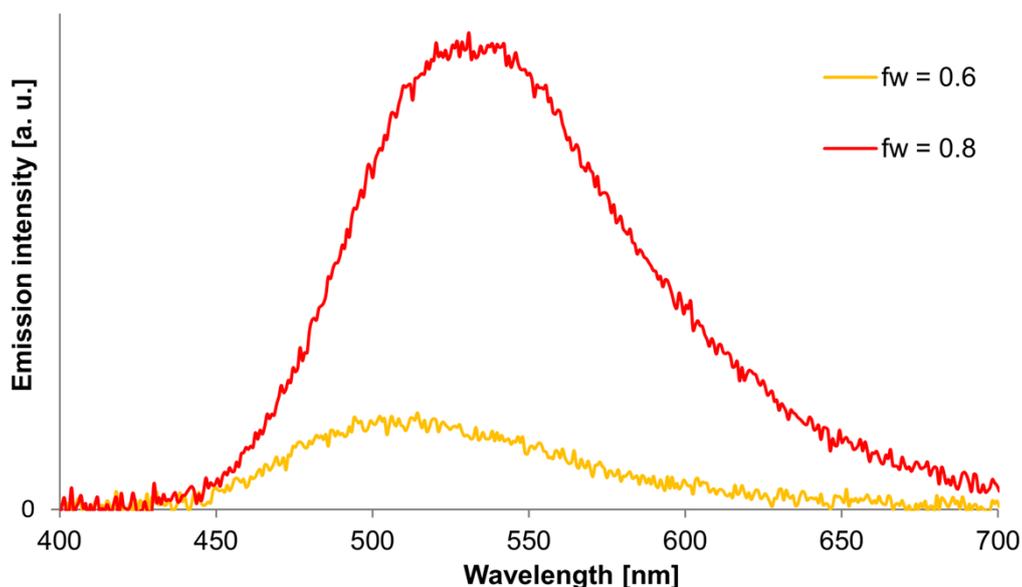


Figure S10. Emission spectra of **5** in DMF/water measured in Hamamatsu Photonics Quantaurus QY (integrating sphere and multi-channel analyzer).

S5. Photophysical properties of 1,1'-binaphthyl in solution and aggregation state

1,1'-binaphthyl was synthesized by Suzuki-Miyaura coupling between 1-iodonaphthalene and 1-naphthaleneboronic acid as explained below. Obtained ^1H NMR, ^{13}C NMR and melting point accorded with the previous report.⁸

1,1'-binaphthyl

A mixture of toluene 15ml, ethanol 6 ml, and water 3ml was deaerated through argon bubbling and subsequently added to a mixture of 1-naphthaleneboronic acid (0.40 g, 2.33 mmol), 1-iodonaphthalene (0.54 g, 2.12 mmol), potassium carbonate (0.88 g, 6.35 mmol), and tetrakis(triphenylphosphine)palladium(0) (122 mg, 0.11 mmol) under argon atmosphere. After the reaction mixture was stirred for 15 min at room temperature, the temperature of the reaction mixture was raised to 110 °C and stirred for 12 h. The reaction mixture was quenched by cooling to room temperature and then extracted with chloroform, and washed with water and brine. Then, the combined organic layer was dried over MgSO_4 . The solvent was removed in *vacuo*, and the residue was purified by silica gel column chromatography on silica gel (hexane:chloroform = 3:1). After subsequent recrystallisation from hexane, 1,1'-binaphthyl (0.38 g) was obtained as a colorless powder. Yield : 70%; Mp: 143.3-143.8 °C; ^1H NMR (300 MHz, CDCl_3): 7.96-7.93 (m, 4H), 7.61-7.56 (m, 2H), 7.50-7.44 (m, 4H), 7.40-7.38 (m, 2H), 7.30-7.25 (m, 2H) ppm.; ^{13}C NMR (75 MHz, CDCl_3): δ 138.5, 133.6, 132.9, 128.2, 127.9, 127.9, 126.6, 126.0, 125.8, 125.4 ppm.

In the measurement of UV-Vis absorption and fluorescence spectra of 1,1'-binaphthyl in THF/water system, solute concentration was fixed to 0.99×10^{-4} M regardless of volume fraction of water f_w . Absorption maxima λ_{abs} and fluorescence maxima λ_{em} in THF solution ($f_w = 0$) corresponded to literature data.⁹ When THF solution of 1,1'-binaphthyl ($f_w = 0$) was diluted to one-half (O.D. = 0.5) or one-tenth (O.D. = 0.1), their absolute PL quantum yield Φ_F hardly changed. As depicted in Figure S10, significant broadening of absorption band in $f_w = 0.8$ indicated aggregation formation. However, fluorescence spectra (Figure S11) and absolute PL quantum yield Φ_F (Table S2) revealed that 1,1'-binaphthyl does not show any enhancement of quantum yields Φ_F with aggregation.

Table S2. Spectroscopic parameters of 1,1'-binaphthyl in THF/water system

Entry	λ_{abs} [nm]	λ_{em} [nm]	λ_{em} [nm] in QY ^{a)}	Φ_{F}
<i>fw</i> = 0 (O.D. \approx 1.0)	294	362	360	0.59
<i>fw</i> = 0 (O.D. \approx 0.5)	-	-	361	0.58
<i>fw</i> = 0 (O.D. \approx 0.1)	-	-	357	0.53
<i>fw</i> = 0.8 (O.D. \approx 1.0)	283	364	365	0.52

a) The fluorescence maxima were obtained in QY measurement.

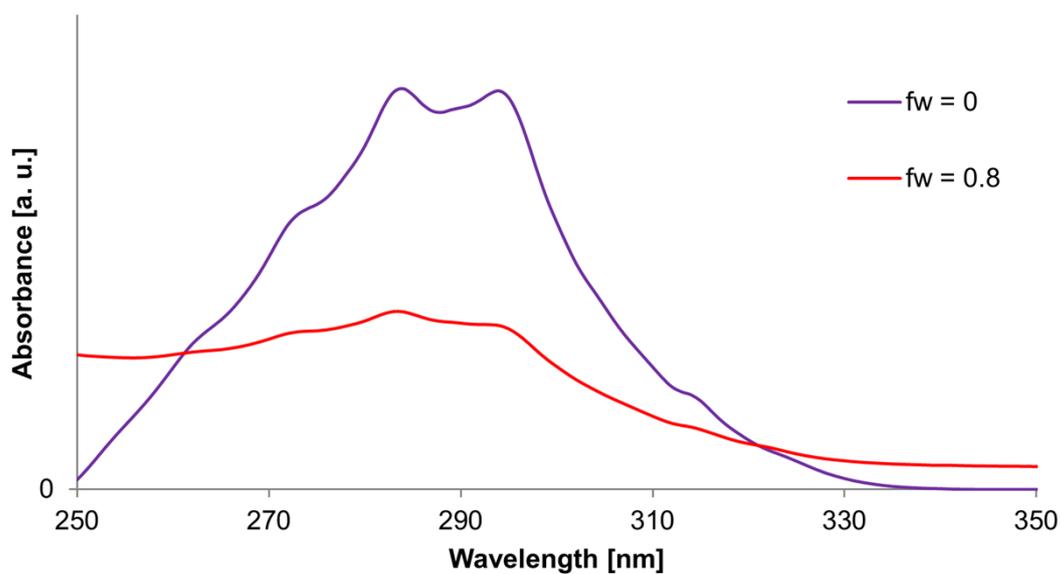


Figure S11. UV-Vis spectrum of 1,1'-binaphthyl in THF/water system.

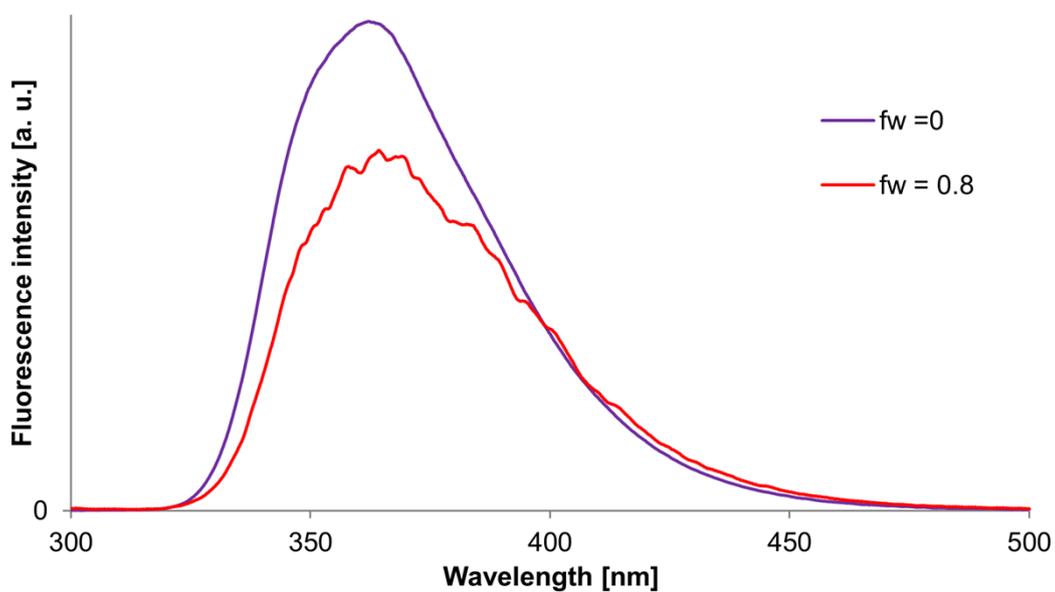


Figure S12. Fluorescence spectrum of 1,1'-binaphthyl in THF/water system.

For comparison with the AIE activity measurement of **5**, UV-Vis absorption and fluorescence spectra of 1,1'-binaphthyl were also obtained in DMF. The solute concentration was fixed to 1.01×10^{-4} M, regardless of the volume fraction of water, f_w . Since the absorption band of DMF overlaps with the absorption maxima, λ_{abs} , of 1,1'-binaphthyl, the quantum yields, Φ_F , obtained by the standard method,¹⁰ in which a vacant quartz cell is used as the reference sample, largely depend on the molar ratio of 1,1'-binaphthyl to DMF (Table S3). When the cell filled with the background solvent is used as the reference sample, the Φ_F values are almost the same, regardless of the optical density of the solute. Under the latter condition, the absolute values of Φ_F tend to be larger than Φ_F obtained by the standard method. However, it can be said that Φ_F at $f_w = 0.8$ is relatively smaller than that at $f_w = 0$.

Table S3. Spectroscopic parameters of 1,1'-binaphthyl in DMF/water system.

Entry	λ_{abs} [nm]	λ_{em} [nm]	λ_{em} [nm] in QY ^{a)}	Φ_F ^{b)}	Φ_F ^{c)}
$f_w = 0$ (O.D. ≈ 1.0)	284	367	367	0.57	0.91
$f_w = 0$ (O.D. ≈ 0.5)	-	-	365	0.52	0.94
$f_w = 0$ (O.D. ≈ 0.1)	-	-	362	0.36	0.92
$f_w = 0.8$ (O.D. ≈ 1.0)	293	370	367	0.55	0.56

a) The fluorescence maxima were obtained by QY measurement. b) The vacant cell was used as the reference sample. c) The cell filled with solvent (DMF or DMF/water with $f_w = 0.8$) was used as the reference sample.

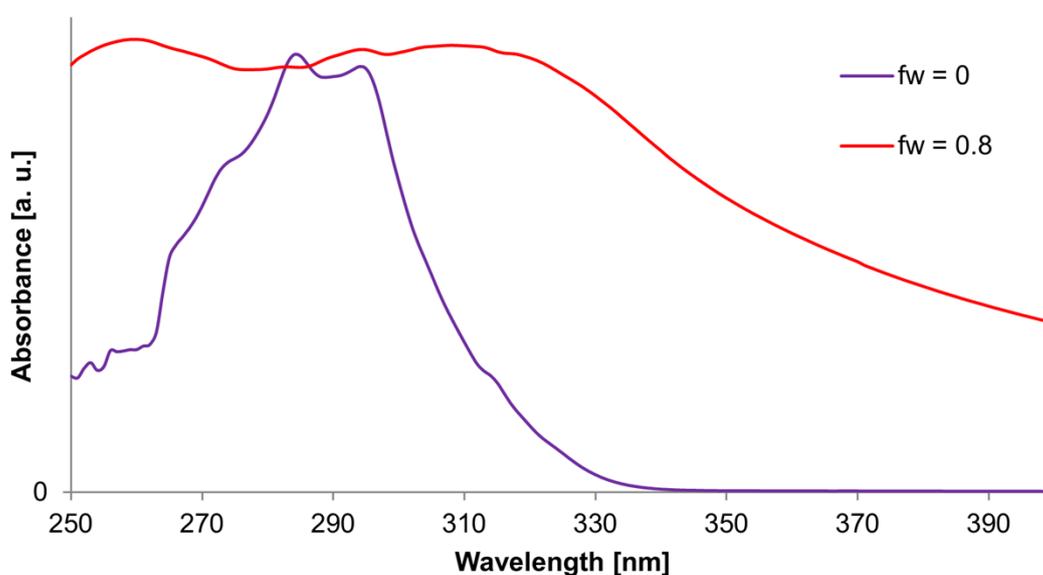


Figure S13. UV-Vis spectrum of 1,1'-binaphthyl in DMF/water system.

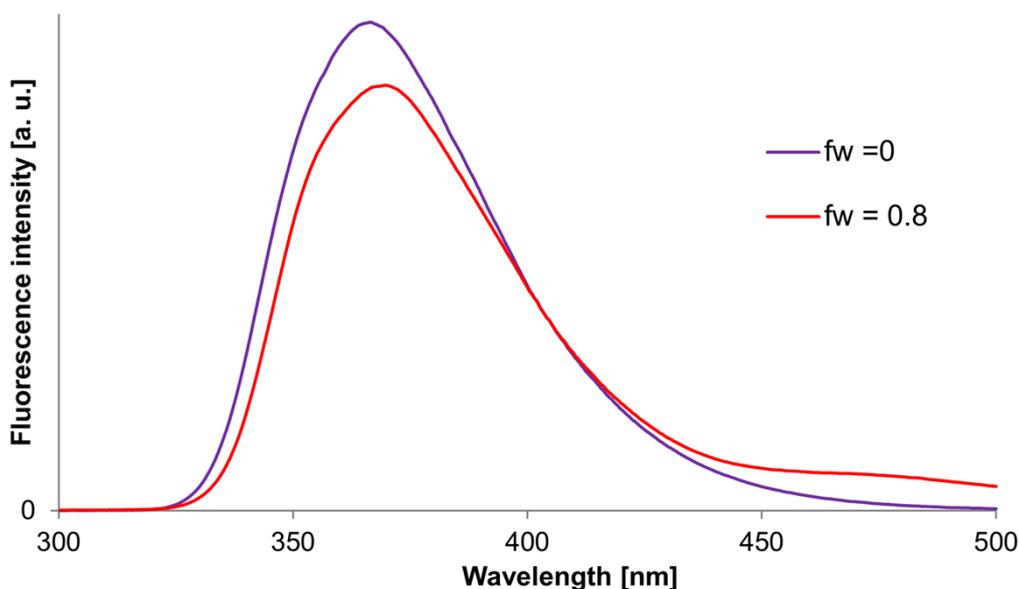


Figure S14. Fluorescence spectrum of 1,1'-binaphthyl in DMF/water system.

S6. Crystallographic informations of 4-formyl-4'-piperidyl-1,1'-binaphthyl 5

Selected crystal data of **5**: monoclinic, $P2_1/n$ (No. 14), $a = 9.789(2)$ Å, $b = 6.437(1)$ Å, $c = 29.940(6)$ Å, $\beta = 96.75(2)^\circ$, $V = 1873.6(6)$ Å³, $Z = 4$, $R_1 = 0.0361$, $wR_2 = 0.0659$.

CCDC 1006100 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S7. References

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