Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

## Supporting information

# *Blackening aza-BODIPY derivatives by simple dimerization: panchromatic absorption of pyrrolopyrrole aza-BODIPY dimer*

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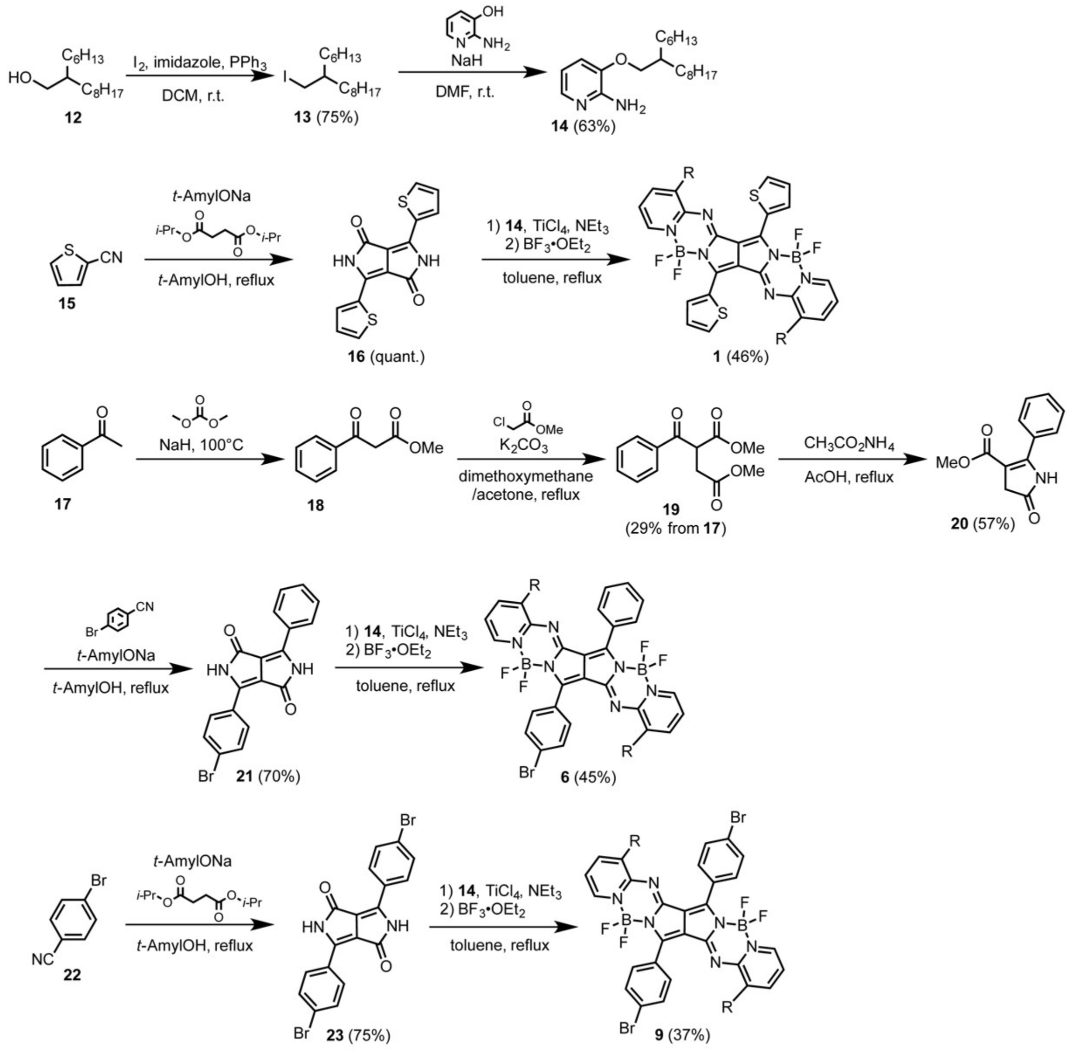
**Contents:**

## i. Synthesis of precursors



**Scheme S1.** Synthetic scheme of starting PPAB monomers, **1**, **6** and **9**.

**2-Hexyl-1-iododecane (13):** 2-Hexyl-1-decanol **12** (8.0 mL, 28 mmol), triphenylphosphine (8.8 g, 32 mmol) and imidazole (2.3 g, 34 mmol) were dissolved in 40 mL of dichloromethane and cooled to 0 ºC under continuous stirring. Subsequently iodine (8.2 g, 32 mmol) was added. The resultant solution was stirred for another 15 min at 0 ºC and then at room temperature for 24 h. The reaction mixture was poured into an aqueous solution of sodium thiosulfate. Organic layer was extracted, and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography using hexane as an eluent to provide **13** as colorless oil (7.4 g, 75%).

$^1$H NMR (CDCl$_3$, 500 MHz, 295 K): $\delta$ [ppm] = 3.27 (d, $J$ = 4.5 Hz, 2H), 1.45-1.00 (m, 25H), 0.93-0.83 (m, 6H).

**2-Amino-3-(2-hexyldecyloxy)pyridine (14): 14** was synthesized according to the literature procedure with slight modification.[1] A mixture of 2-amino-3-hydroxypyridine (1.9 g, 18 mmol) and activated sodium hydride (0.58 g, 26 mmol) was stirred in dry DMF (30 mL) at room temperature for 1 h under $N_2$. Then a solution of **13** (7.4 g, 21 mmol) in dry DMF (4 mL) was added, and the reaction mixture was stirred for 24 h at room temperature in the dark. The reaction mixture was poured into water and extracted with chloroform. The crude product was purified by silica gel column chromatography using hexane as an eluent to remove residual DMF and then using methanol as an eluent to afford **14** as dark brown oil (3.67 g, 63%). This compound was used in the next step without further purification.

$^1$H NMR ($CDCl_3$, 500 MHz, 295K): $\delta$[ppm] = 7.62 (d, $J$ = 5.3 Hz, 1H), 6.88 (d, $J$ = 8.3 Hz, 1H), 6.59 (dd, $J_1$ = 7.9 Hz, $J_2$ = 4.9 Hz, 1H), 4.65 (br, 2H), 3.84 (d, $J$ = 5.3 Hz, 2H), 1.83-1.75 (m, 1H), 1.48-1.17 (m, 24H), 0.92-0.82 (m, 6H).

**3,6-Di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (16):** Sodium (0.83 g, 36 mmol) and a small amount of iron(III) chloride was added to *t*-amyl alcohol (66 mL), and the mixture was refluxed. After sodium was dissolved, **15** (3.0 mL, 32 mmol) was added to the refluxing solution. Diisopropylsuccinate (2.2 mL, 11 mmol) was added dropwise to the reaction mixture over 10 h, and the reaction mixture was refluxed for further 12 h. After the reaction mixture was allowed to cool to r.t., 35% aqueous HCl solution (0.6 mL) and methanol were added. The mixture was stored overnight in a refrigerator. The precipitate was filtered and washed with methanol and water to afford **16** as a dark red solid (3.3 g, quant.).

$^1$H NMR (DMSO-$d_6$, 500 MHz, 295 K): $\delta$[ppm] = 11.24 (s, 2H), 8.21 (d, $J$ = 3.8 Hz, 2H), 7.96 (d, $J$ = 5.3 Hz, 2H), 7.33-7.27 (m, 2H).

**1: 16** (0.60 g, 2.0 mmol) and **14** (3.0 g, 9.0 mmol) were added to a dry toluene (45 mL), and the mixture was refluxed. Titanium tetrachloride (1.2 mL, 11 mmol) was added to the reaction mixture. After 10 min, triethylamine (4.0 mL, 29 mmol) was added. When formation of imine was confirmed by TLC analysis after ca. 1.5 h, borontrifluoride etherate (3.8 mL, 31 mmol) was added, and the resultant mixture was refluxed overnight. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane. The combined organic extracts were dried over sodium sulfate and concentrated in vacuo to give a green solid. The crude residue was purified by silica gel column chromatography (dichloromethane/hexane = 1:2 (v/v)) to provide **1** as a green solid (0.93 g, 46%).

$^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$[ppm] = 9.46 (s, 2H), 7.95 (s, 2H), 7.77 (s., 2H), 7.32 (m, 4H), 7.13 (d, $J$ =

6.6 Hz, 2H), 4.04 (d, *J* = 5.1 Hz, 4H), 2.07 (d, *J* = 6.3 Hz, 2H), 1.56-1.27 (m, 48H), 0.85 (t, *J* = 2.1 Hz, 12H); UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ [nm] ($\varepsilon$ [$M^{-1}cm^{-1}$]) = 306 (28000), 383 (28000), 436 (21000), 465 (14000), 631 (37000), 693 (108000); $\Phi_F$ = 0.42 ($CHCl_3$).

**2-Benzoylacetic acid methyl ester (18): 18** was synthesized according to the literature procedure with slight modification.[2] Activated sodium hydride (2.6 g, 110 mmol) in dimethyl carbonate (66 mL) was heated up to 100 °C. **17** (8.7 g, 72 mmol) dissolved in dimethyl carbonate (12 mL) was added dropwise to the solution over 40 min under vigorous stirring. After stirring for a further 30 min at the same temperature, the solution was allowed to cool to r.t. After addition of methanol (33 mL) and acetic acid (5.5 mL), the mixture was extracted twice with dichloromethane, washed with water, and concentrated in vacuo. The crude product was dried under reduced pressure to yield **18** as crude yellow oil (10 g, less than 79% yield, not completely pure). This mixture was used in the next step without further purification.

**2-Benzoylmaleic acid dimethyl ester (19): 19** was synthesized according to the literature procedure with slight modification.[2] A mixture of **18** (10 g, ca. 62 mmol), methyl-2-chloroacetate (4.4 g, 41 mmol), potassium carbonate (5.5 g, 40 mmol) and dimethoxymethane (15 mL) in acetone (39 mL) was refluxed for 20 h. After cooling to r.t., the suspension was filtered, and the residual salts were washed with *t*-butyl methyl ether. The organic filtrates were combined, and the solvent was removed under reduced pressure. The residue was purified twice by silica gel column chromatography (dichloromethane/hexane = 1:1 (v/v)) to provide **19** as yellow oil (7.3 g, 29% from **17**).

$^1H$ NMR (500 MHz, $CDCl_3$, 291 K): $\delta$ [ppm] = 8.04 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 2H), 4.91-4.88 (m, 1H), 3.69 (t, *J* =2.3 Hz, 6H), 3.08 (m, 2H).

**2-Phenyl-3-methoxycarbonyl-2-pyrrolin-5-one (20): 20** was synthesized according to the literature procedure with slight modification.[2] Ammonium acetate (25 g, 600 mmol) and **19** (7.3 g, 55 mmol) were refluxed in acetic acid (53 mL) for 3.5 h (oil-bath temperature: 125 °C). After cooling to r.t., ice water was added to the solution with vigorous stirring. The precipitates were filtered, dried under vacuum, and purified by silica gel column chromatography (dichloromethane/methanol = 95:5 (v/v)) to yield **20** as white solids (3.6 g, 57%).

$^1H$ NMR (500 MHz, $CDCl_3$, 291 K): $\delta$ [ppm] = 7.59 (d, *J* = 7.9 Hz, 2H), 7.47 (m, 4H), 3.67 (s, 3H), 3.52 (s, 2H).

**3-(4-Bromophenyl)-6-phenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (21):** **21** was synthesized according to the literature procedure with slight modification.[3] Sodium (0.46 g, 20 mmol) and a small amount of iron(III) chloride were added to *t*-amyl alcohol (48 mL) at 110 °C, and then the mixture was refluxed. After sodium was dissolved, *p*-bromobenzonitrile (1.4 g, 7.4 mmol) and **20** (1.4 g, 5.3 mmol) were added to the mixture. After refluxing for 4 h, acetic acid and methanol were added to the reaction mixture. The resultant mixture was filtered and washed with methanol to provide **21** as dark red solids (1.4 g, 70%).
$^1$H NMR (500 MHz, DMSO-$d_6$, 295 K): $\delta$ [ppm] = 11.38 (br, 2H), 8.48 (m, 2H), 8.41 (d, $J$ = 8.5 Hz, 2H), 7.81 (d, $J$ = 8.5 Hz, 2H), 7.58 (m, 3H).

**6:** **21** (100 mg, 0.27 mmol) and **14** (0.45 g, 1.4 mmol) were added to a dry toluene (8.5 mL) and the mixture was refluxed. Titanium tetrachloride (0.16 mL, 1.5 mmol) and triethylamine (0.54 mL, 3.8 mmol) were successively added. After 1 h, the imine formation was confirmed by TLC analysis, and then borontrifluoride etherate (0.49 mL, 4.1 mmol) was added. After additional refluxing for 6 h, the reaction mixture was poured into water and extracted with dichloromethane. The combined organic extracts were dried over sodium sulfate and concentrated in vacuo to give blue solids. The crude compound was purified by silica gel column chromatography (dichloromethane/hexane = 1:1 (v/v)) to afford **6** as a blue solid (135 mg, 45%).
$^1$H NMR (500 MHz, $CD_2Cl_2$, 294 K): $\delta$ [ppm] = 8.43-8.33 (m, 2H), 8.28 (d, $J$ = 9.1 Hz, 2H), 7.83 (t, $J$ = 5.7 Hz, 2H), 7.66 (d, $J$ = 8.3 Hz, 2H), 7.60-7.40 (3H), 7.27 (t, $J$ = 7.9 Hz, 2H), 7.14-6.98 (m, 2H), 3.96 (d, $J$ = 5.3 Hz, 2H), 3.92 (d, $J$ = 5.3 Hz, 2H), 1.98-1.80 (m, 2H), 1.57-1.00 (48H), 0.91-0.76 (m, 12H).

**3,6-Bis(4-bromophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (23):** Sodium (1.8 g, 79 mmol) and a small amount of iron(III) chloride were added to *t*-amyl alcohol (30 mL) at 90 °C, and then the mixture was refluxed. After sodium was dissolved, **22** (7.33 g, 41 mmol) was added to the mixture. Then diisopropylsuccinate (5.0 mL, 24 mmol) in *t*-amyl alcohol (12 mL) was added dropwise over 20 h. The mixture was allowed to cool to 60 °C, and acetic acid (4.6 mL, 80 mmol) and MeOH (30 mL) were added. The resultant precipitates were filtered and washed with water and methanol to provide **23** as dark red solids (8.0 g, 18 mmol, 75%).
$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ [ppm] = 11.4 (br, 2H), 8.43 (d, $J$ = 8.4 Hz, 4H), 8.23 (d, $J$ = 8.4 Hz, 4H).

**9:** **23** (440 mg, 1.0 mmol) and **14** (1.5 g, 4.5 mmol) were added to a dry toluene (30 mL), and the mixture was refluxed. Then titanium tetrachloride (0.60 mL, 5.4 mmol) and triethylamine (2.0 mL, 14 mmol) were added to the reaction mixture. After the imine formation was confirmed by TLC analysis, borontrifluoride etherate (1.8 mL, 15 mmol) was added. After refluxing for further 14 h, the reaction mixture was added to water (60 mL) and extracted with dichloromethane. The combined organic extracts were dried over sodium sulfate and concentrated in vacuo to provide blue solids. The crude compound was chromatographed on silica gel column (dichloromethane/hexane = 1:2 (v/v)) to afford **9** as blue solids (433 mg, 37%).

$^1$H NMR (500 MHz, $CDCl_3$, 295 K): $\delta$ [ppm] = 8.34 (d, $J$ = 9.5 Hz, 4H), 7.87 (d, $J$ = 6.0 Hz, 2H), 7.65 (d, $J$ = 8.5 Hz, 4H), 7.25 (d, $J$ = 9.5 Hz, 2H), 7.05 (dd, $J$ = 6.0 Hz, $J$ = 8.0 Hz 2H).

## ii. $^1$H NMR and H-H COSY Spectra

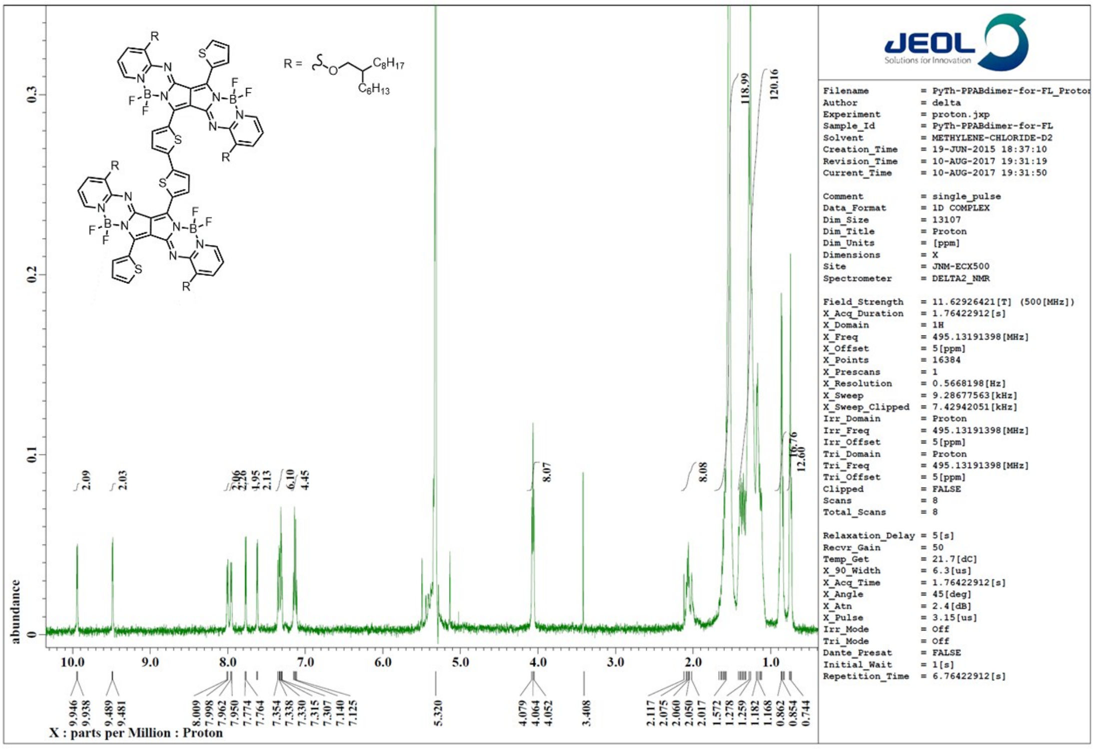


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**Fig. S1.** $^1$H NMR Spectrum of **3.**

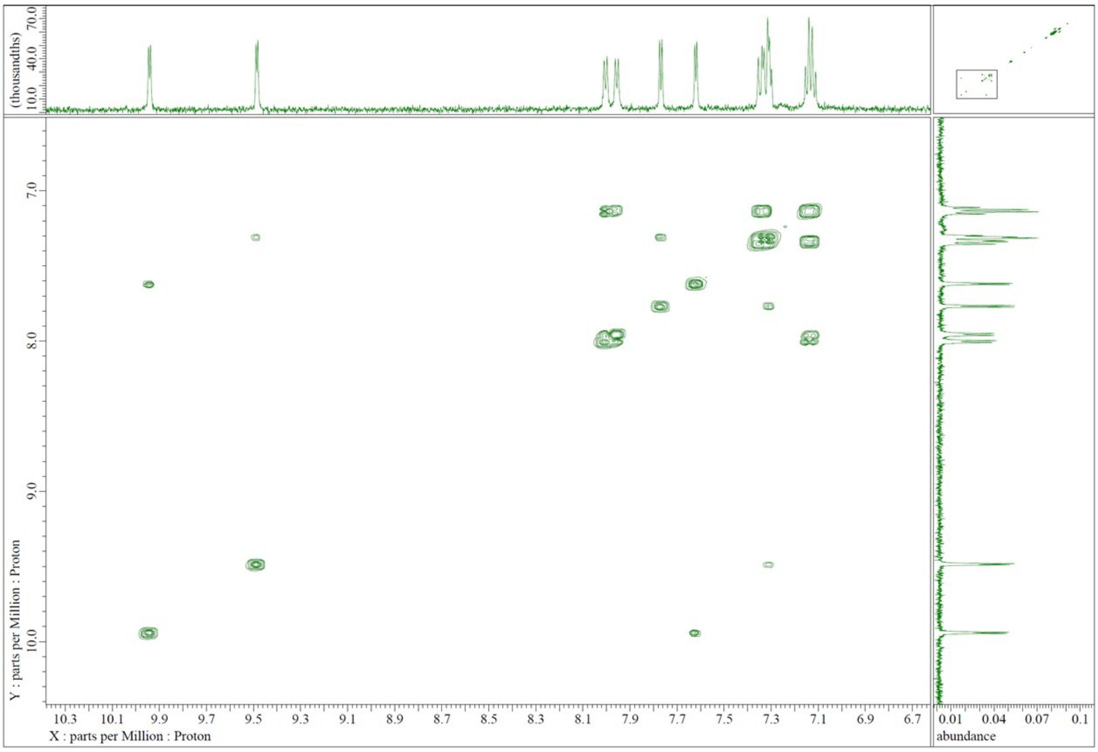

**Fig. S2.** H-H COSY spectrum of **3**.

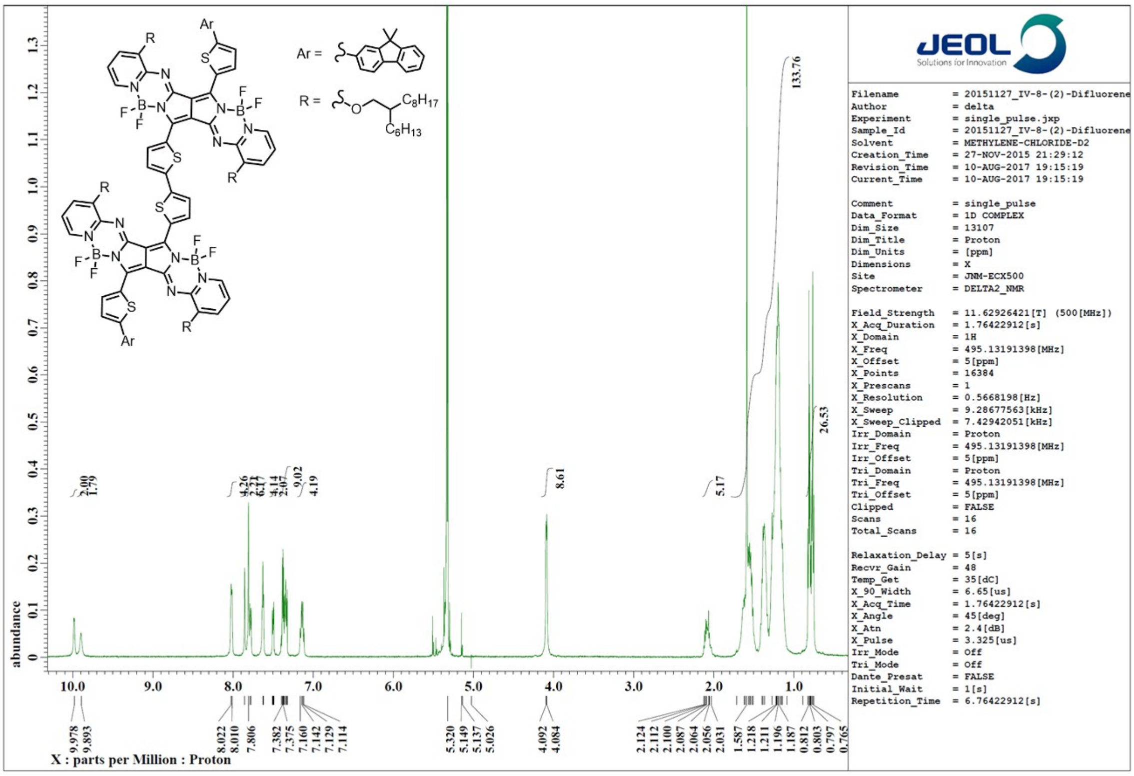

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**Fig. S3.** $^1$H NMR Spectrum of **4**.

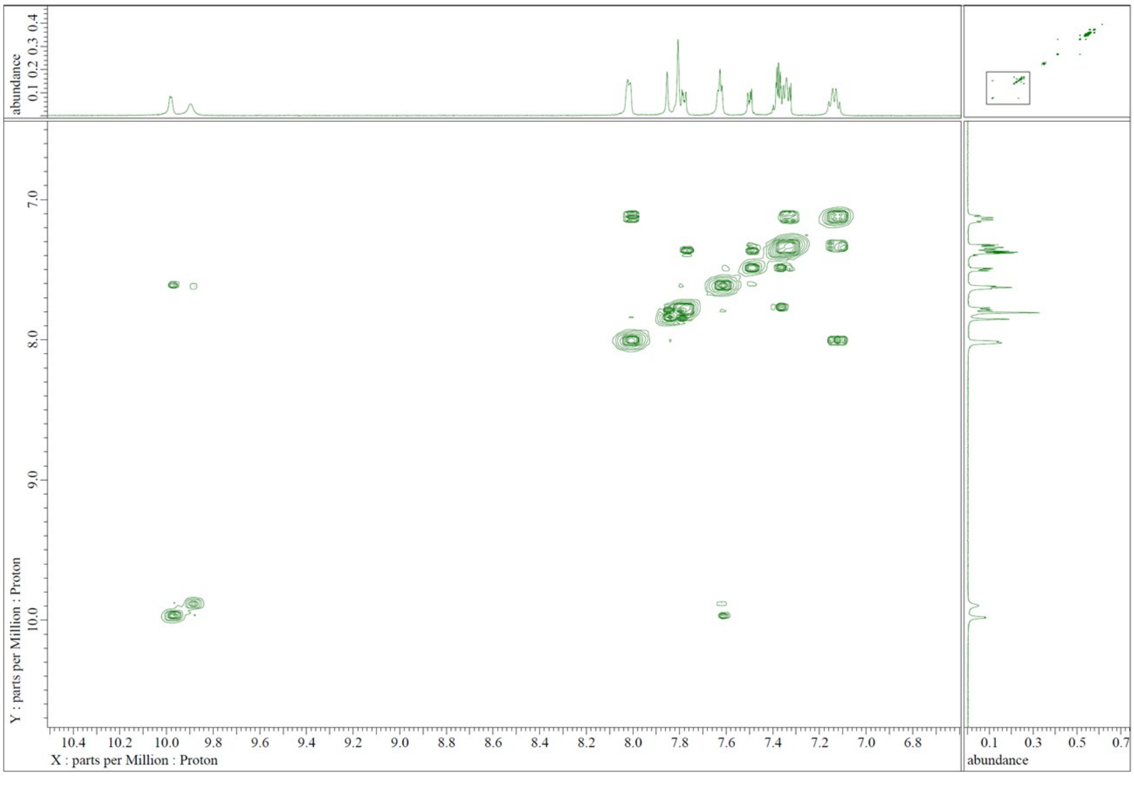

**Fig. S4.** H-H COSY spectrum of **4**.

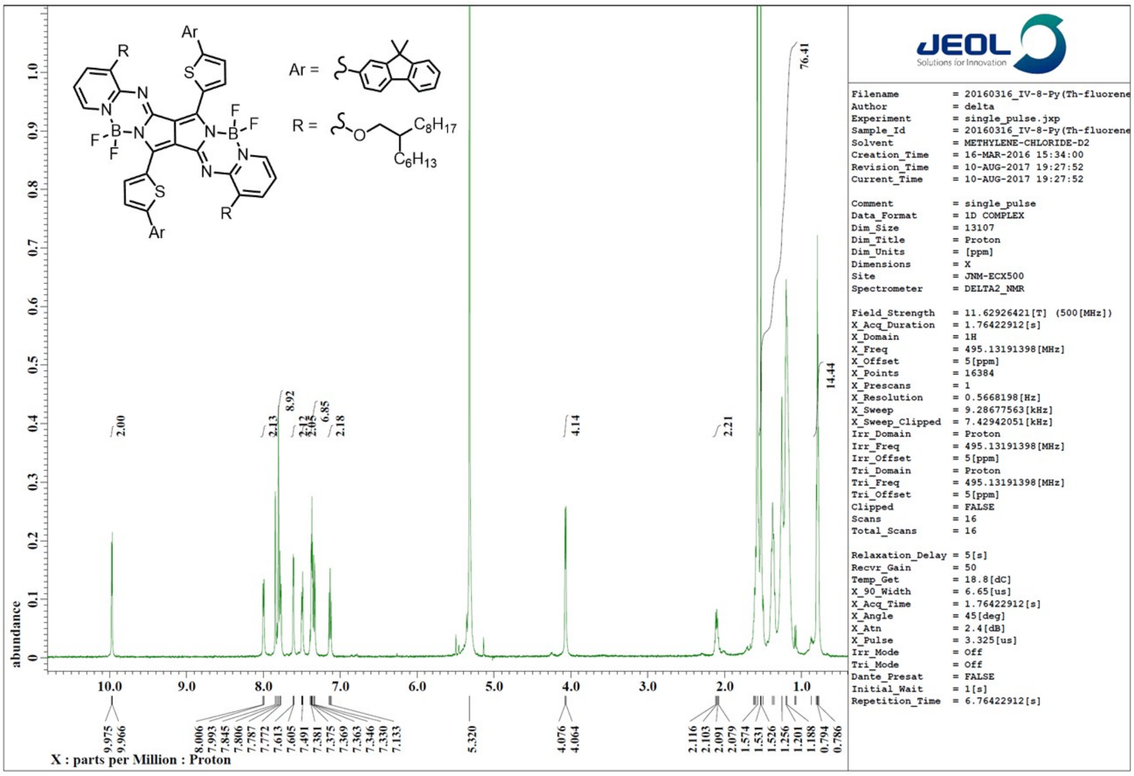

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**Fig. S5.** $^1$H NMR Spectrum of **5**.

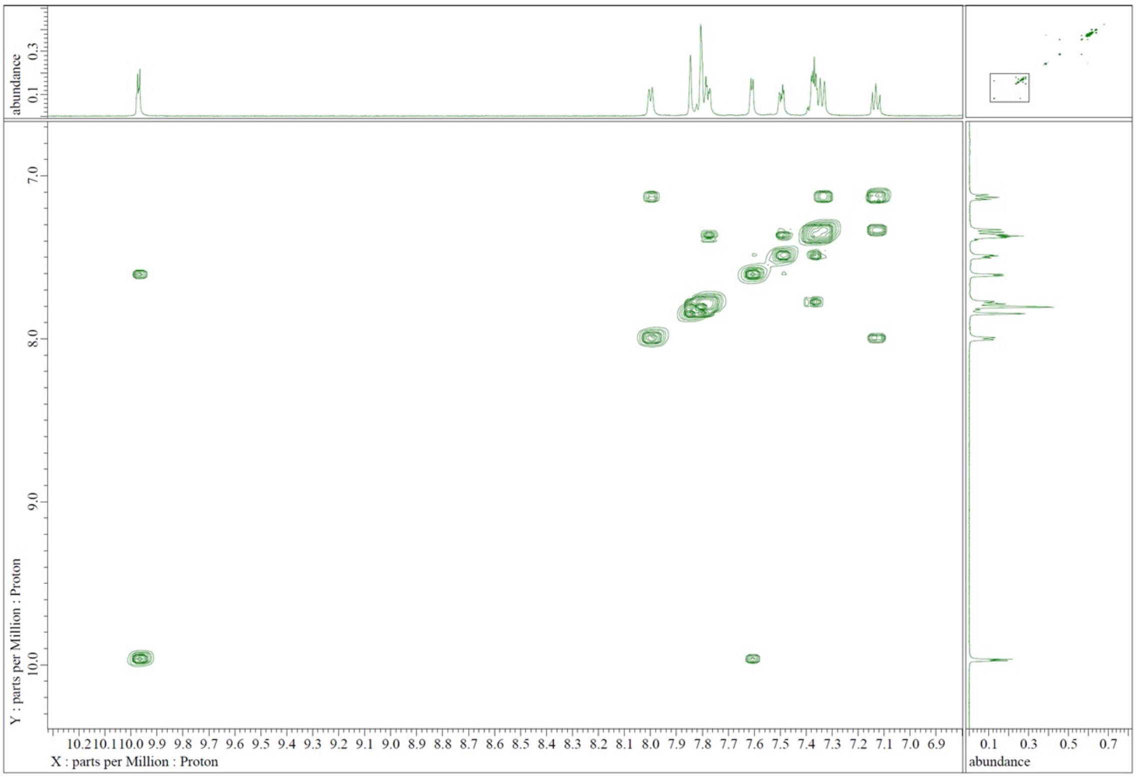

**Fig. S6.** H-H COSY spectrum of **5**.

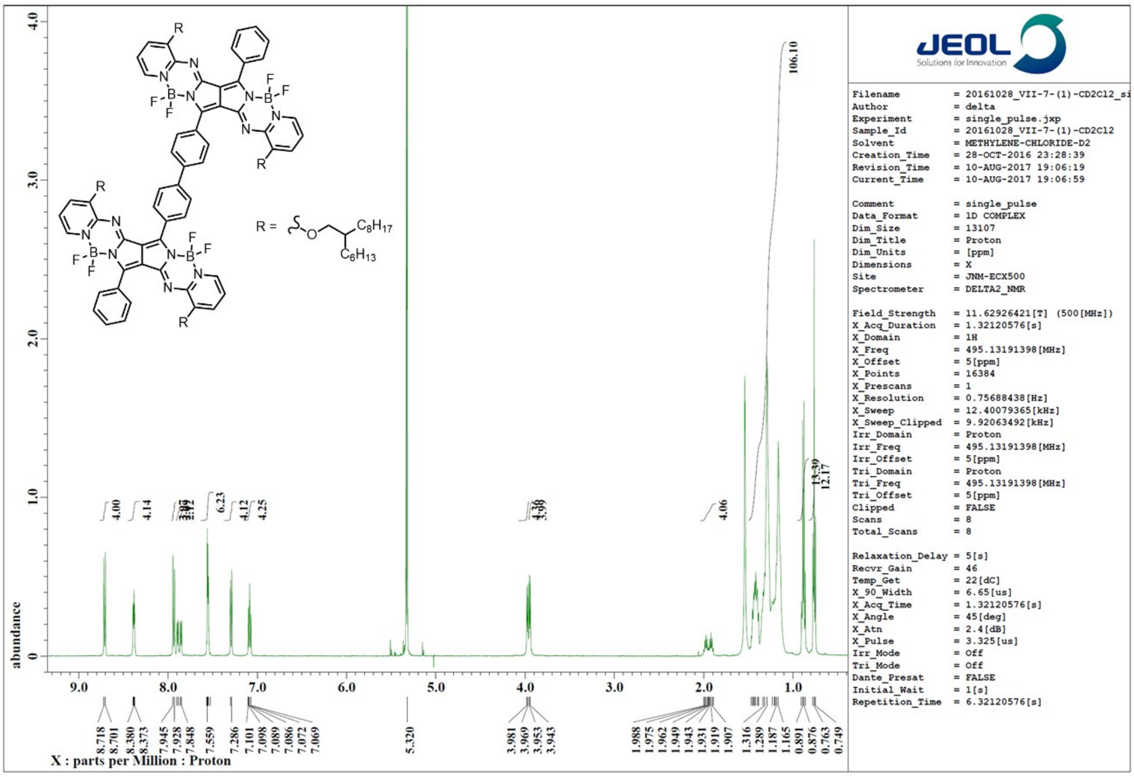

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**Fig. S7.** $^1$H NMR Spectrum of **8**.

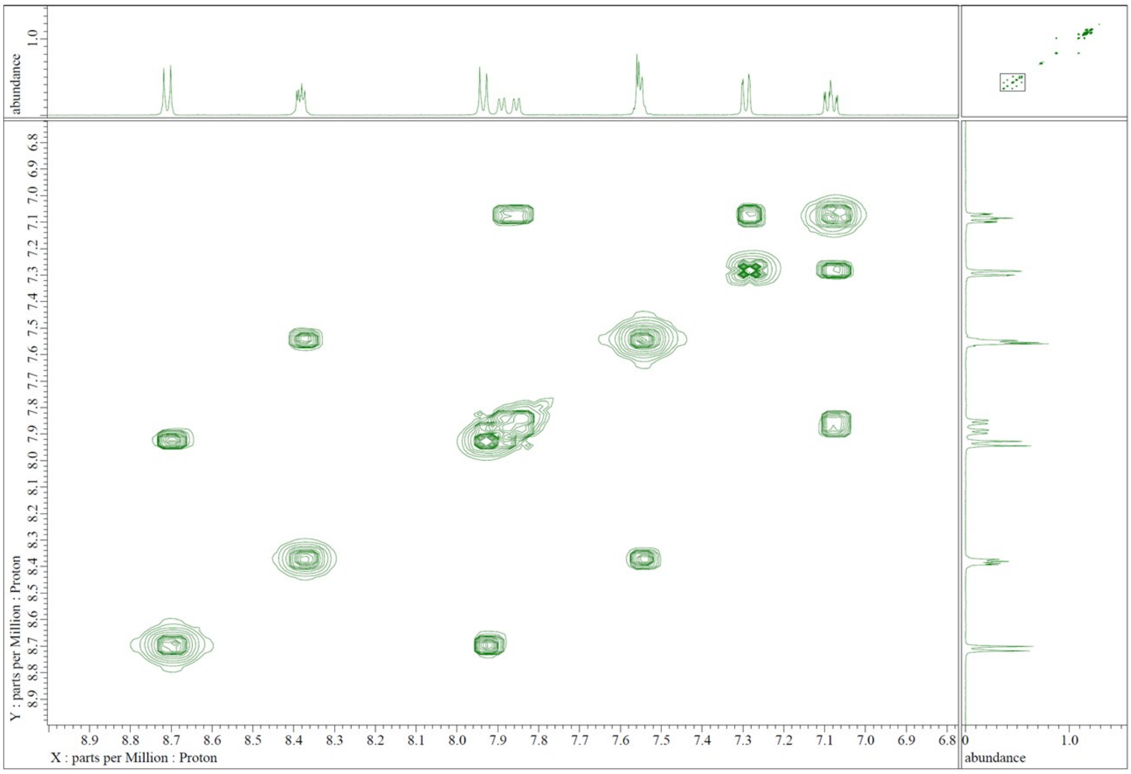

**Fig. S8.** H-H COSY spectrum of **8**.

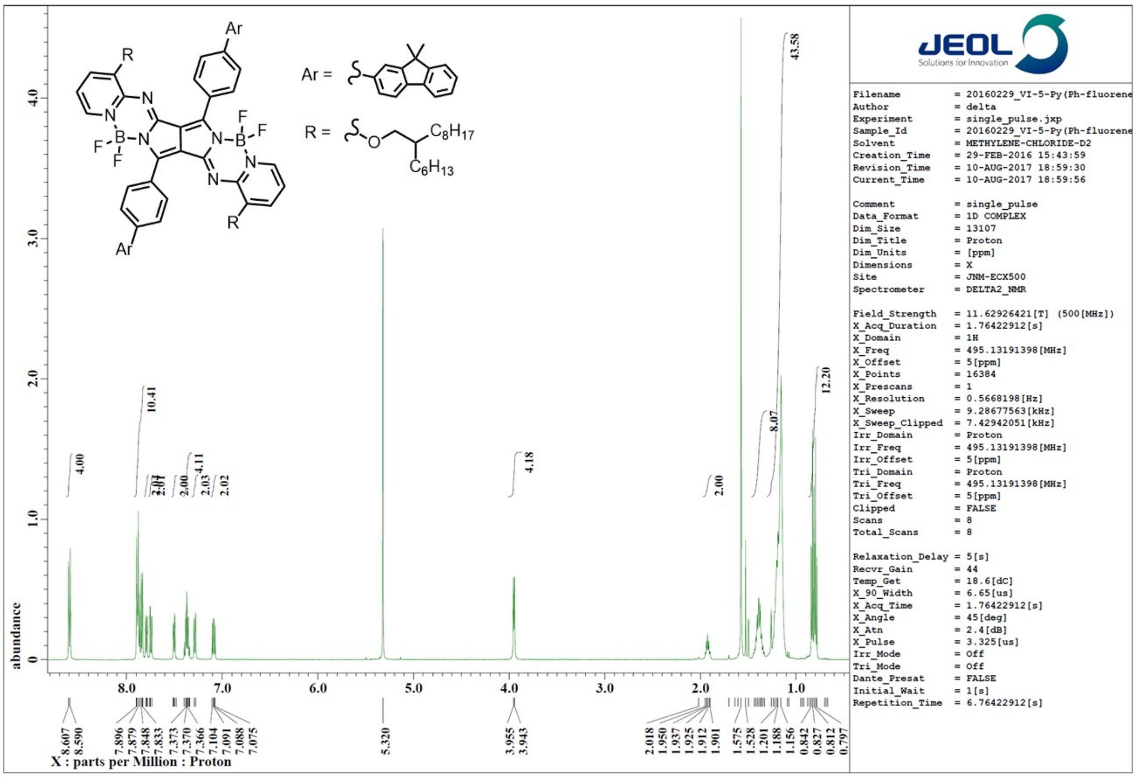

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**Fig. S9.** $^1$H NMR Spectrum of **10**.

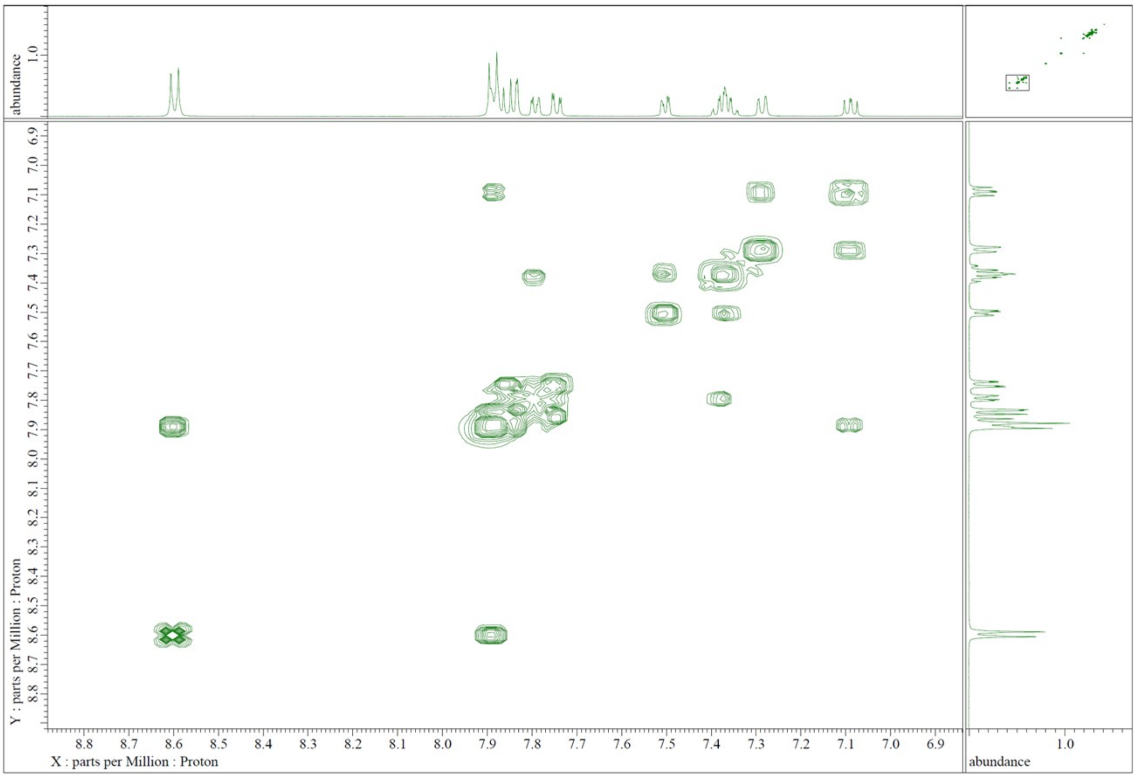
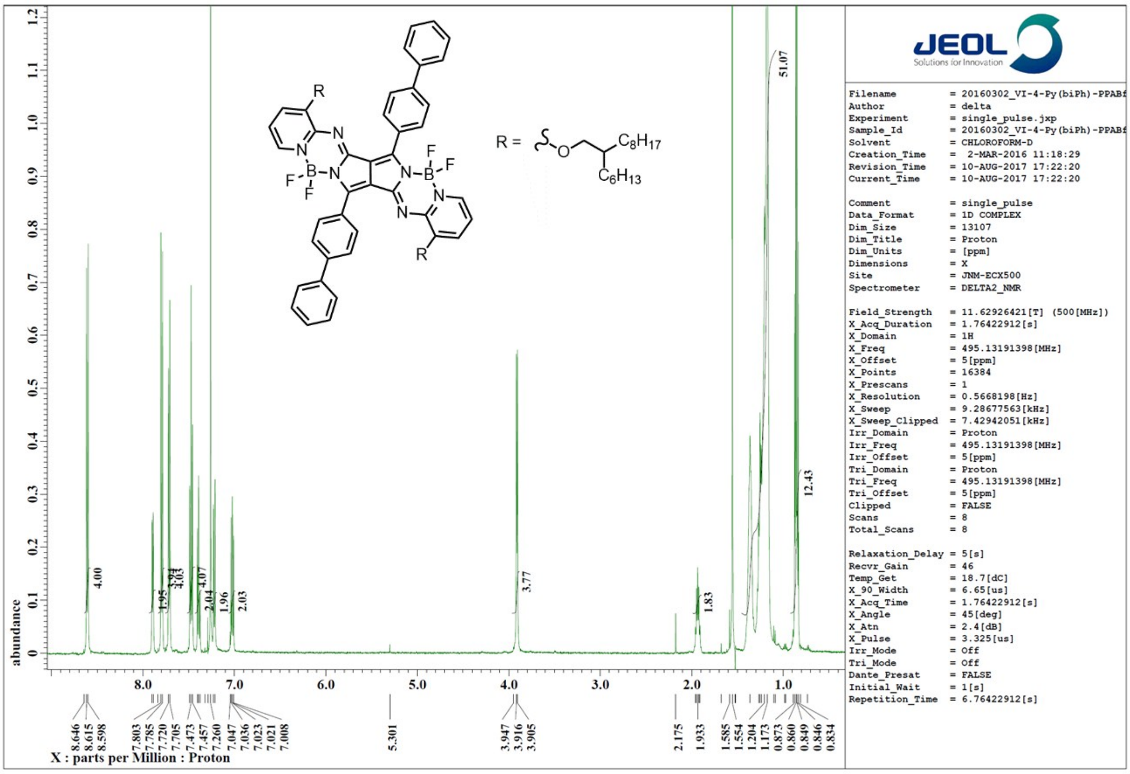


**Fig. S10.** H-H COSY spectrum of **10**.



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Author             = delta
Experiment         = single_pulse.jxp
Sample_Id          = 20160302_VI-4-Py(biPh)-PPABf
Solvent            = CHLOROFORM-D
Creation_Time      =  2-MAR-2016 11:18:29
Revision_Time      = 10-AUG-2017 17:22:20
Current_Time       = 10-AUG-2017 17:22:20

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 1.76422912[s]
X_Domain           = 1H
X_Freq             = 495.13191398[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.5668198[Hz]
X_Sweep            = 9.28677563[kHz]
X_Sweep_Clipped    = 7.42942051[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Proton
Tri_Freq           = 495.13191398[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
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Total_Scans        = 8

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Recvr_Gain         = 46
Temp_Get           = 18.7[dC]
X_90_Width         = 6.65[us]
X_Acq_Time         = 1.76422912[s]
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X_Atn              = 2.4[dB]
X_Pulse            = 3.325[us]
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Dante_Presat       = FALSE
Initial_Wait       = 1[s]
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**Fig. S11.** $^1$H NMR Spectrum of **11**.

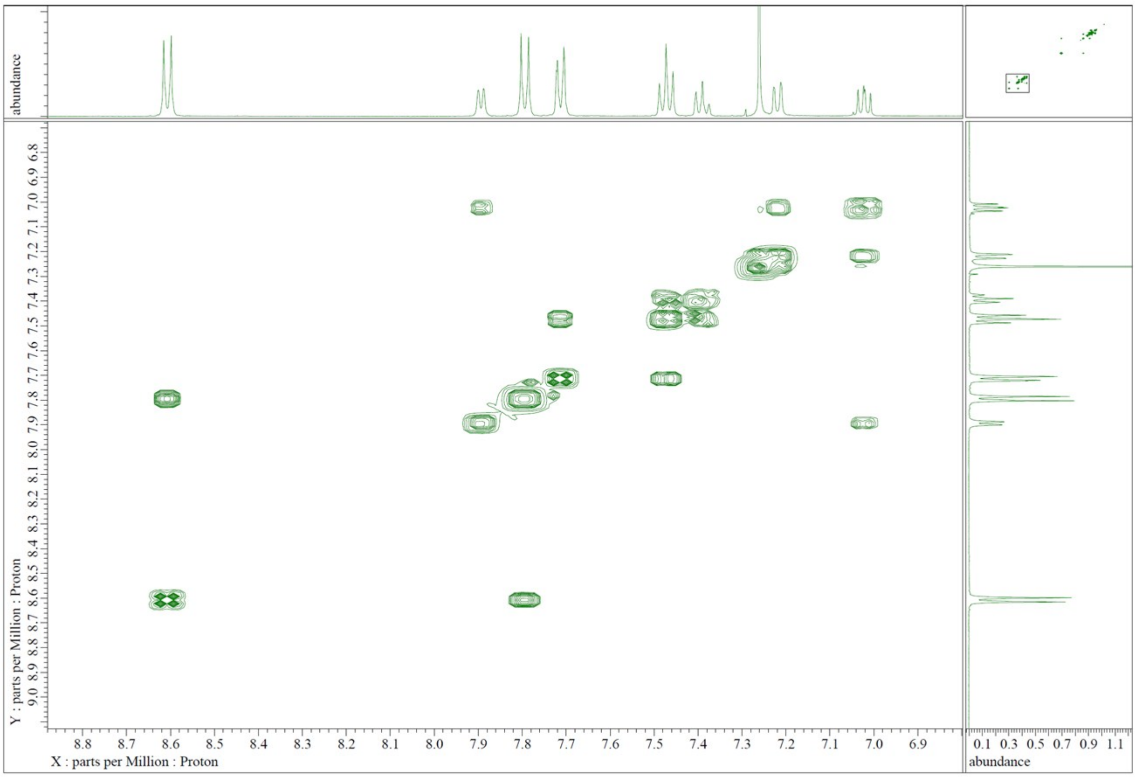

**Fig. S12.** H-H COSY spectrum of **11**.

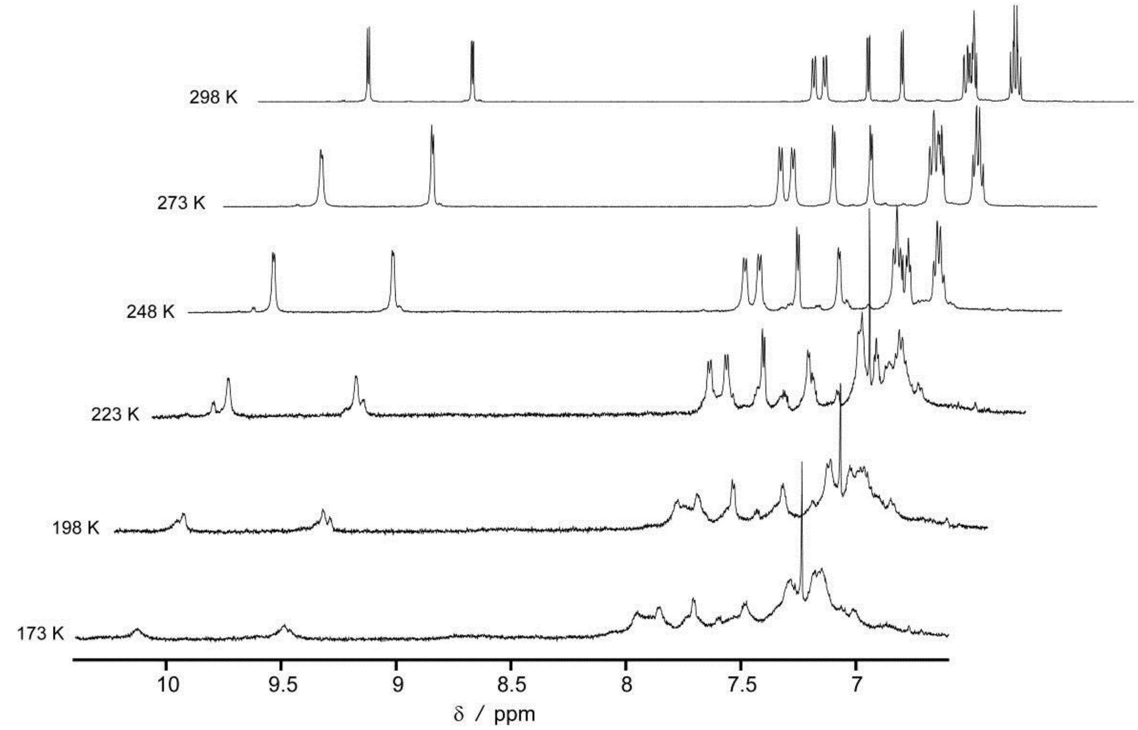

**Fig. S13.** Variable temperature $^1$H NMR spectra of **3** in $CD_2Cl_2$.

### iii. X-ray Single Crystal Structures

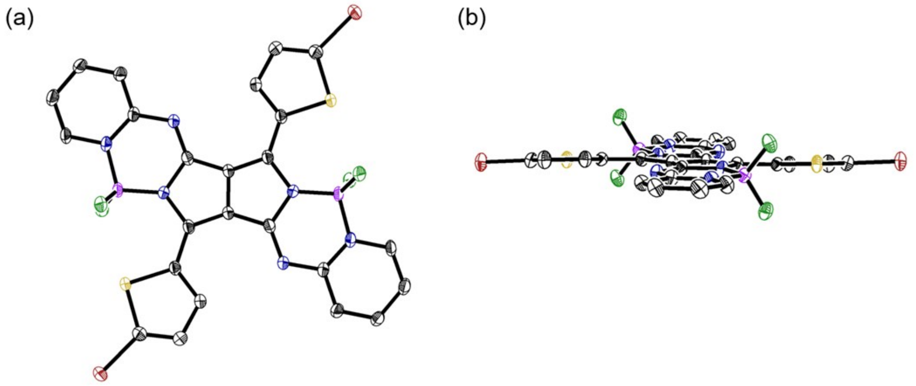

**Fig. S14.** X-ray single crystal structure of **2**. (a) Top view and (b) side view in which alkoxy substituents and hydrogen atoms were omitted for clarity. The thermal ellipsoids were scaled to 50% probability level.

**Table S1.** Crystallographic data of **2**.

| | |
|---|---|
| Empirical formula | $C_{56}H_{76}B_2Br_2F_4N_6O_2S_2$ |
| Formula weight | 1186.78 |
| Crystal system, Space group | Triclinic, *P*-1 (no. 2) |
| Temperature (K) | 100.15 |
| Wavelength (Å) | 0.71069 ($Mo_{K\alpha}$) |
| *a*, *b*, *c* (Å) | 8.451(5), 12.572(5), 14.826(5) |
| $\alpha, \beta, \gamma$ (°) | 72.872(5), 77.851(5), 78.602(5) |
| Volume ($Å^3$) | 1456.0(11) |
| *Z* | 1 |
| Density (calcd.) ($g/cm^3$) | 1.353 |
| $\mu$ ($mm^{-1}$) | 1.522 |
| F(000) | 618 |
| Crystal size ($mm^3$) | 0.20 × 0.12 × 0.02 |
| $\theta$ (°) for data collection | 1.934 to 24.99 |
| Index ranges | $-10 \leq h \leq 10, -14 \leq k \leq 14, -17 \leq l \leq 17$ |
| Reflections collected | 19879 |
| Unique reflections | 5121 ($R_{int} = 0.0486$) |
| Completeness | 0.999 |
| Absorption correction | Multi-scan |
| Data/restrains/parameters | 5121/0/336 |
| Goodness-of-fit on $F^2$ | 1.06 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.058 |
| *wR*2 indices (all data) | 0.158 |
| Large diff. peak and hole | 0.83, –0.66 |
| CCDC number | 1572423 |

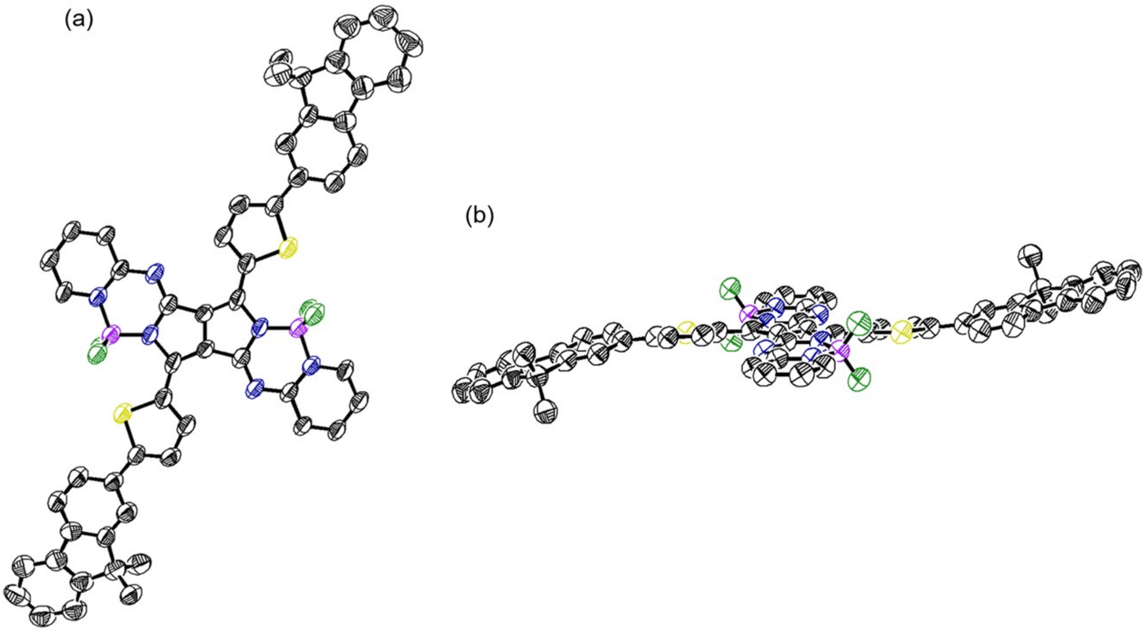

**Fig. S15.** X-ray single crystal structure of **5**. (a) Top view and (b) side view in which alkoxy substituents and hydrogen atoms were omitted for clarity. The thermal ellipsoids were scaled to 50% probability level.

**Table S2.** Crystallographic data of **5**.

| | |
|---|---|
| Empirical formula | $C_{86}H_{102}B_2F_4N_6O_2S_2$ |
| Formula weight | 1413.47 |
| Crystal system, Space group | Triclinic, *P*-1 (no. 2) |
| Temperature (K) | 100.15 |
| Wavelength (Å) | 1.54187 ($Cu_{K\alpha}$) |
| *a*, *b*, *c* (Å) | 8.4567(4), 10.5402(5), 21.6860(11) |
| $\alpha$, $\beta$, $\gamma$ (°) | 82.021(6), 88.740(6), 76.218(5) |
| Volume (Å$^3$) | 1859.03(16) |
| *Z* | 1 |
| Density (calcd.) (g/cm$^3$) | 1.263 |
| $\mu$ (mm$^{-1}$) | 1.154 |
| F(000) | 754 |
| Crystal size (mm$^3$) | 0.27 × 0.1 × 0.01 |
| $\theta$ (°) for data collection | 4.117 to 68.209 |
| Index ranges | $-10 \le h \le 10$, $-12 \le k \le 12$, $-26 \le l \le 26$ |
| Reflections collected | 34590 |
| Unique reflections | 6708 ($R_{int}$ = 0.0970) |
| Completeness | 0.986 |
| Absorption correction | Multi-scan |
| Data/restrains/parameters | 6708/270/462 |
| Goodness-of-fit on $F^2$ | 0.916 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.0946 |
| *wR*2 indices (all data) | 0.2752 |
| Large diff. peak and hole | 0.775, –0.329 |
| CCDC number | 1572424 |

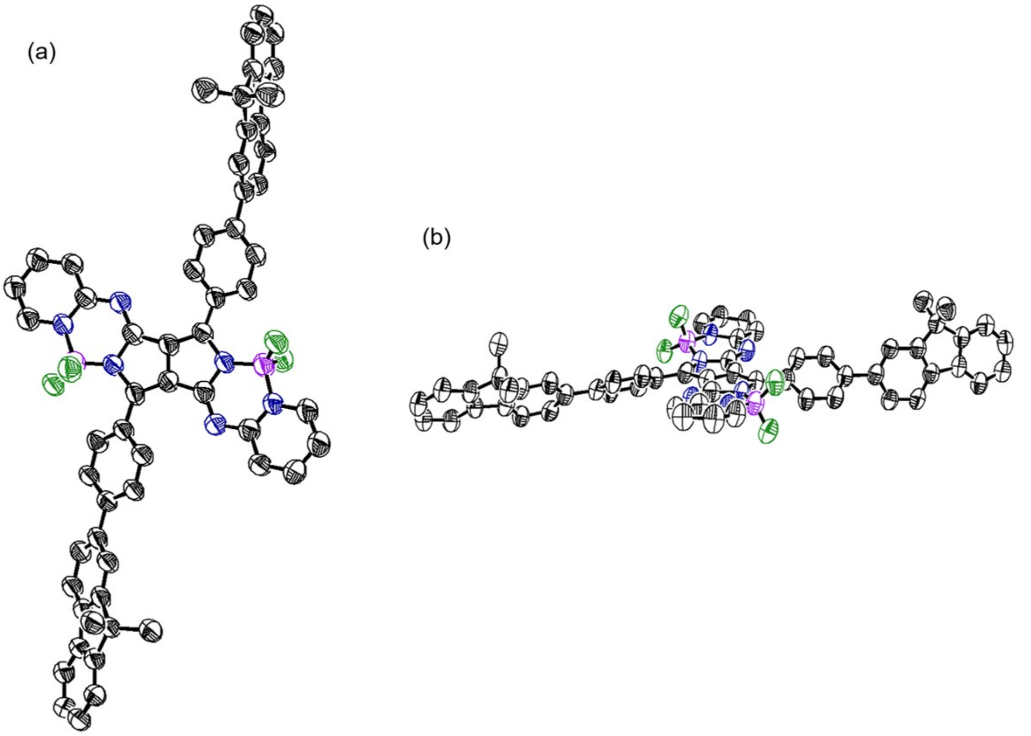

**Fig. S16.** X-ray single crystal structure of **10**. (a) Top view and (b) side view in which alkoxy substituents and hydrogen atoms were omitted for clarity. The thermal ellipsoids were scaled to 50% probability level.

**Table S3.** Crystallographic data of **10**.

| | |
|---|---|
| Empirical formula | $C_{90}H_{106}B_2F_4N_6O_2$ |
| Formula weight | 1401.48 |
| Crystal system, Space group | Triclinic, *P*-1 (no. 2) |
| Temperature (K) | 100.0 |
| Wavelength (Å) | 1.54187 ($Cu_{K\alpha}$) |
| *a*, *b*, *c* (Å) | 14.0940(6), 18.3573(8), 18.6826(9) |
| $\alpha$, $\beta$, $\gamma$ (°) | 61.093(4), 67.847(5), 71.552(5) |
| Volume (Å$^3$) | 3865.1(3) |
| *Z* | 2 |
| Density (calcd.) (g/cm$^3$) | 1.204 |
| $\mu$ (mm$^{-1}$) | 0.615 |
| F(000) | 1500 |
| Crystal size (mm$^3$) | 0.16 × 0.15 × 0.01 |
| $\theta$ (°) for data collection | 3.027 to 68.216 |
| Index ranges | $-16 \leq h \leq 16$, $-21 \leq k \leq 22$, $-22 \leq l \leq 22$ |
| Reflections collected | 71441 |
| Unique reflections | 13901 ($R_{int}$ = 0.0878) |
| Completeness | 0.983 |
| Absorption correction | Multi-scan |
| Data/restrains/parameters | 13901/1012/1332 |
| Goodness-of-fit on $F^2$ | 1.035 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.0962 |
| *wR*2 indices (all data) | 0.2409 |
| Large diff. peak and hole | 0.35, –0.32 |
| CCDC number | 1572425 |

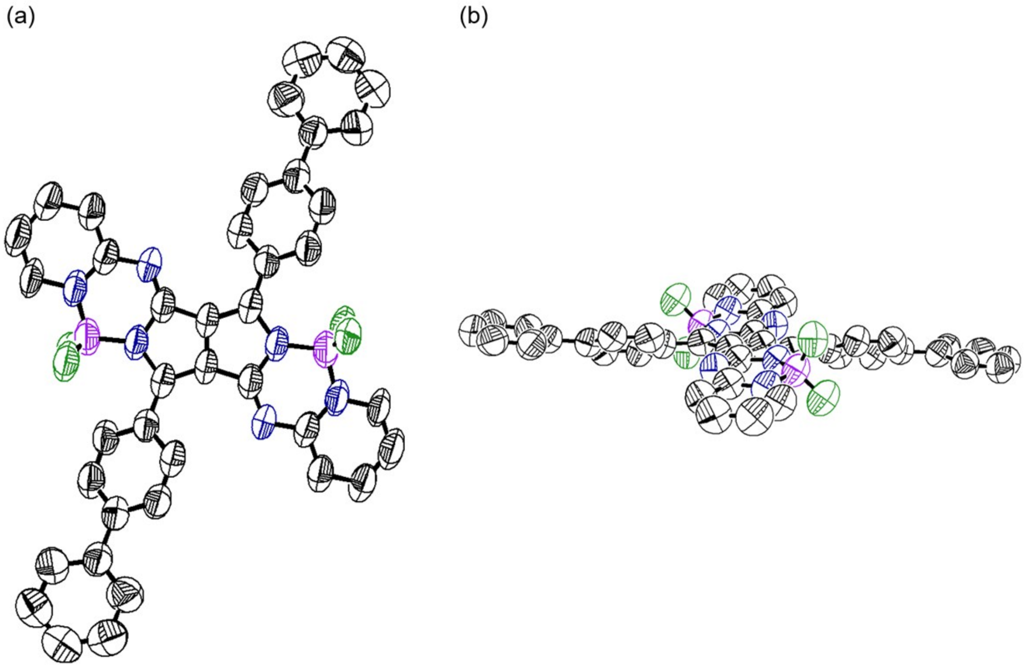

**Fig. S17.** X-ray single crystal structure of **11**. (a) Top view and (b) side view in which alkoxy substituents and hydrogen atoms were omitted for clarity. The thermal ellipsoids were scaled to 50% probability level.

**Table S4.** Crystallographic data of **11**.

| | |
|---|---|
| Empirical formula | $C_{72}H_{90}B_2F_4N_6O_2$ |
| Formula weight | 1169.16 |
| Crystal system, Space group | Triclinic, *P*-1 (no. 2) |
| Temperature (K) | 100.0 |
| Wavelength (Å) | 1.54187 ($Cu_{K\alpha}$) |
| *a*, *b*, *c* (Å) | 9.2398(8), 18.0450(17), 20.6650(19) |
| $\alpha$, $\beta$, $\gamma$ (°) | 71.240(5), 79.325(6), 81.654(6) |
| Volume (Å$^3$) | 3192.4(5) |
| *Z* | 2 |
| Density (calcd.) (g/cm$^3$) | 1.216 |
| $\mu$ (mm$^{-1}$) | 0.643 |
| F(000) | 1252 |
| Crystal size (mm$^3$) | 0.50 × 0.25 × 0.04 |
| $\theta$ (°) for data collection | 3.946 to 68.214 |
| Index ranges | $-11 \leq h \leq 10$, $-21 \leq k \leq 21$, $-24 \leq l \leq 24$ |
| Reflections collected | 60224 |
| Unique reflections | 11473 ($R_{int} = 0.0817$) |
| Completeness | 0.983 |
| Absorption correction | Multi-scan |
| Data/restrains/parameters | 11473/854/1056 |
| Goodness-of-fit on $F^2$ | 1.000 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.0855 |
| *wR*2 indices (all data) | 0.2276 |
| Large diff. peak and hole | 0.28, –0.24 |
| CCDC number | 1572426 |

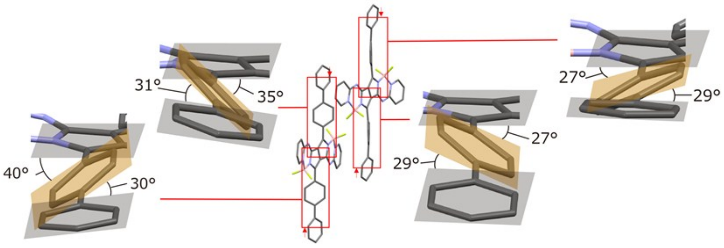

**Fig. S18.** Dihedral angles around the biphenyl groups in the crystal structure of **11**.

### iv. Absorption and fluorescence spectra

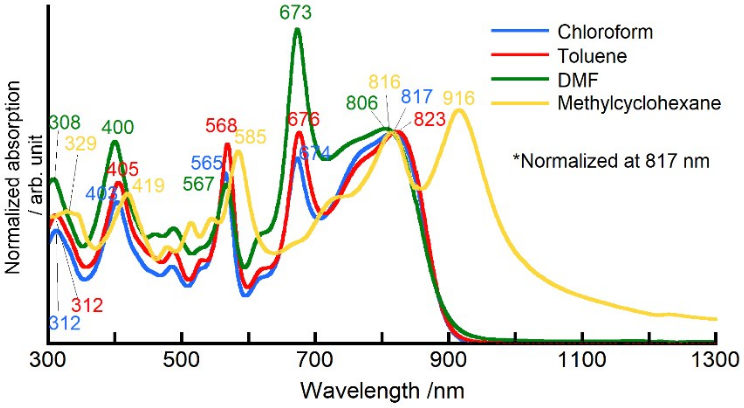

**Fig. S19.** UV/Vis/NIR absorption spectra of **3** in various solvents.

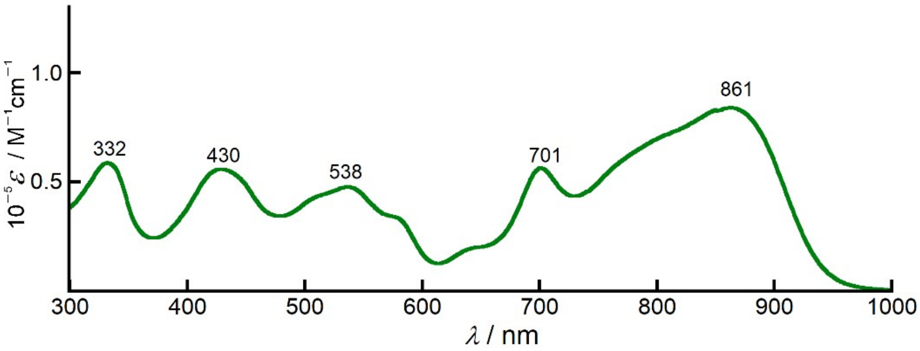

**Fig. S20.** UV/Vis/NIR absorption spectrum of **4** in chloroform.

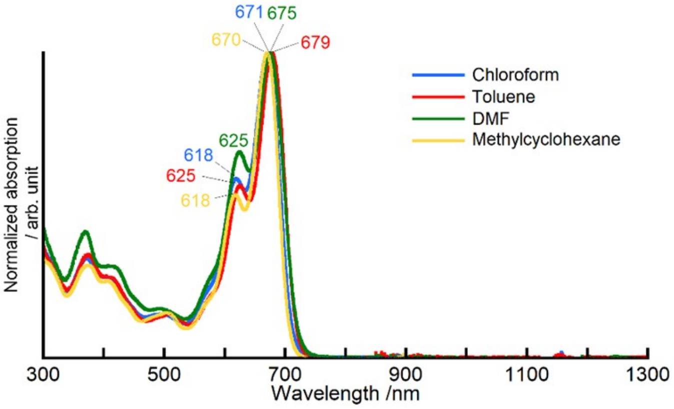

**Fig. S21.** UV/Vis/NIR absorption spectra of **8** in various solvents.

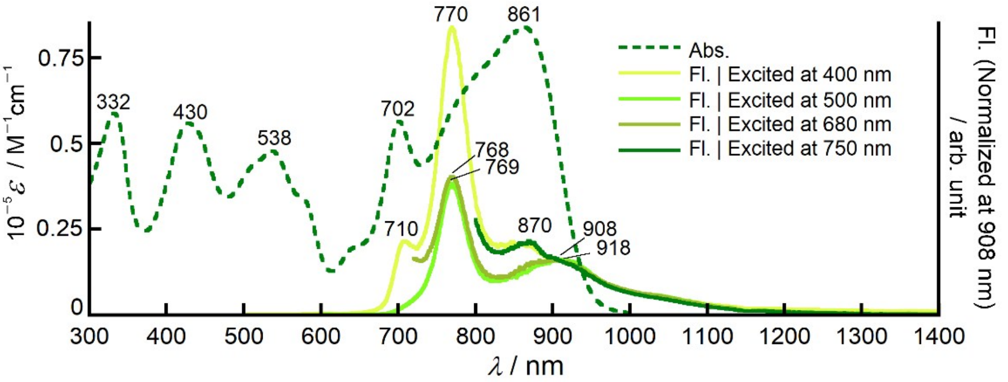

**Fig. S22.** UV/Vis/NIR absorption (top, solid line and bottom, dashed line) and fluorescence (bottom, solid line) spectra of **4** in chloroform. Excitation wavelengths are 400 (yellow green), 550 (emerald green), 630 (moss green), and 700 nm (green).

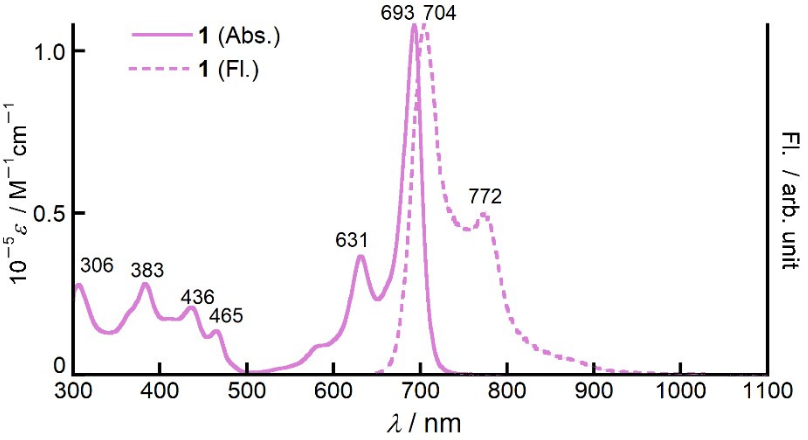

**Fig. S23.** UV/Vis/NIR absorption (solid line) and fluorescence (dashed line) spectra of **1** in chloroform.

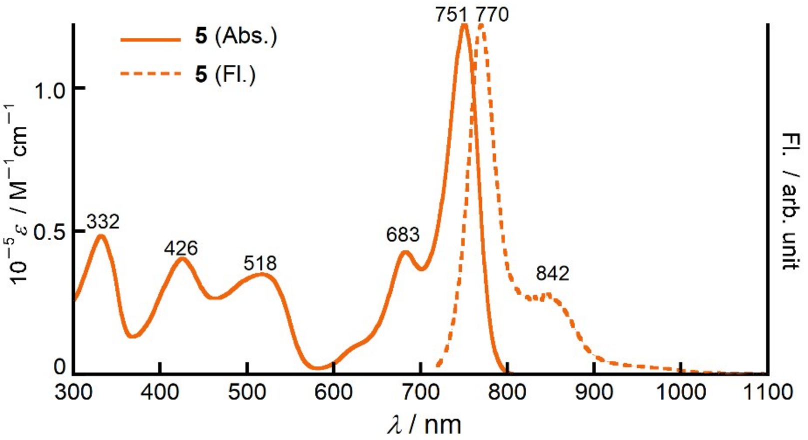

**Fig. S24.** UV/Vis/NIR absorption (solid line) and fluorescence (dashed line) spectra of **5** in chloroform.

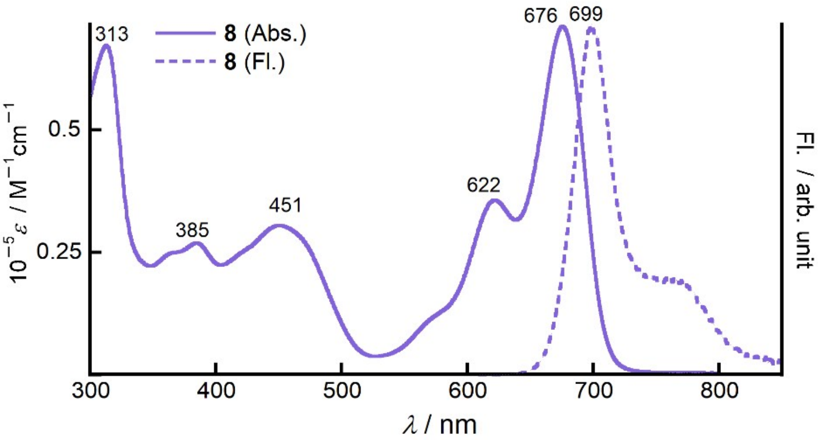

**Fig. S25.** UV/Vis/NIR absorption (solid line) and fluorescence (dashed line) spectra of **10** in chloroform.

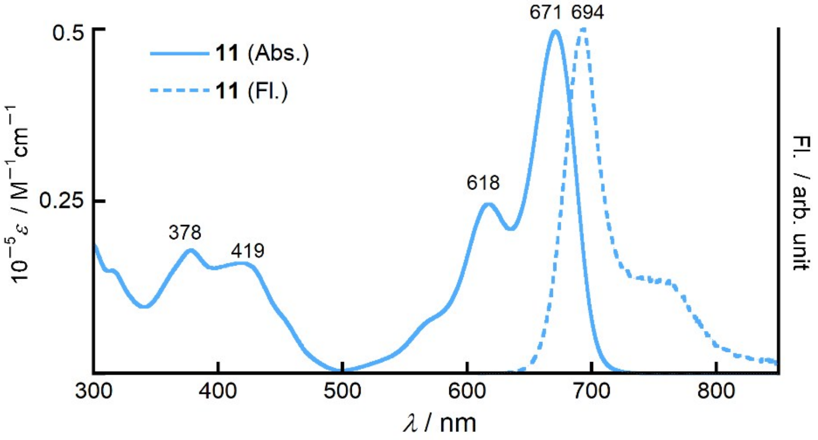

**Fig. S26.** UV/Vis/NIR absorption (solid line) and fluorescence (dashed line) spectra of **11** in chloroform.

## v Optimized structures based on DFT calculation, theoretical absorptions, and molecular orbitals

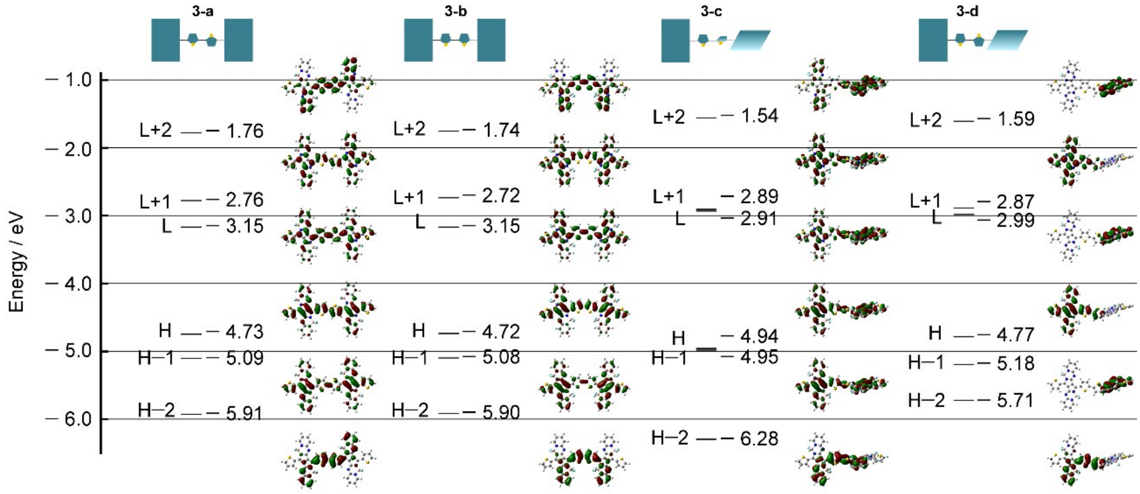

**Fig. S27.** Frontier molecular orbital diagrams of **3** from the HOMO–2 to LUMO+2 at the B3LYP/6-31G(d) level.

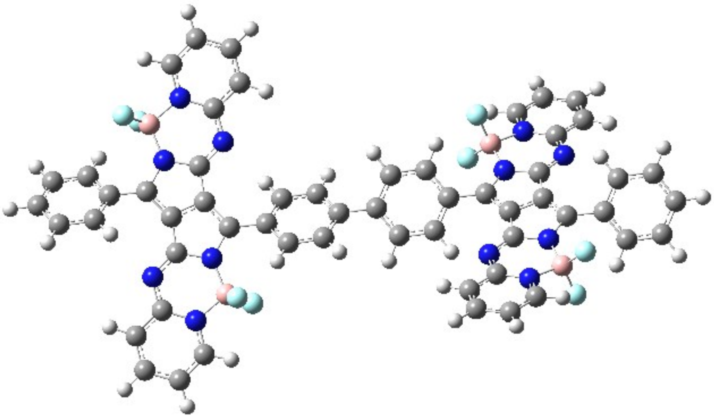

**Fig. S28.** An optimized structure of **8** at the B3LYP/6-31G(d) level. Alkoxy substituents were replaced with hydrogen atoms for simplicity.

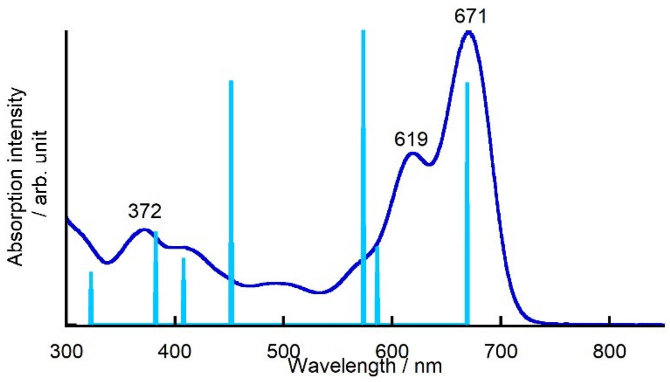

**Fig. S29.** Calculated absorption spectrum of **8** based on the TDDFT method at the B3LYP/6-31G(d) level (aqua blue bars) overlaid on the UV/Vis absorption spectrum of **8** in chloroform.

**Table S5.** Summary of TDDFT calculation of **8** (B3LYP/6-31G(d)).

| $\lambda$ / nm | Oscillator strength | Major contributions |
|---|---|---|
| 669 | 0.57 | H→L (96%) |
| 586 | 0.18 | H–1→L(44%), H→L+1 (58%) |
| 573 | 0.69 | H–1→L+1 (96%) |
| 452 | 0.57 | H–2→L (95%) |
| 408 | 0.15 | H–1→L+3 (15%), H→L+2 (73%) |
| 382 | 0.22 | H–6→L (16%), H–4→L (12%), H→L+4 (41%) |
| 323 | 0.12 | H–12→L (28%), H–1→L+7 (39%) |

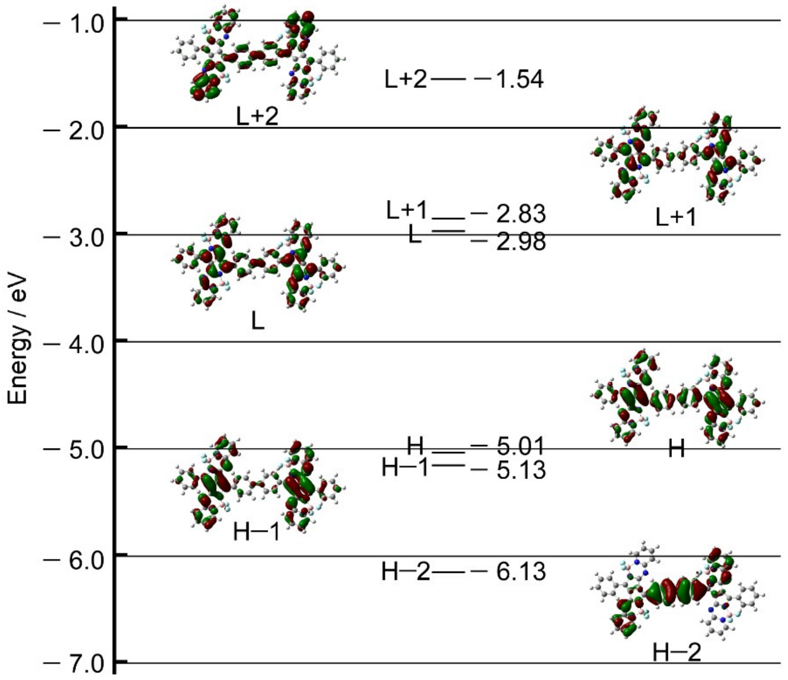

**Fig. S30.** Frontier molecular orbital diagrams of **8** from the HOMO–2 to LUMO+2 at the B3LYP/6-31G(d) level.

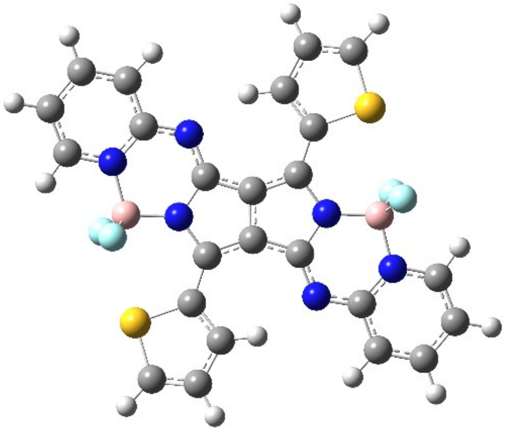

**Fig. S31.** An optimized structure of **1** at the B3LYP/6-31G(d) level. Alkoxy substituents were replaced with hydrogen atoms for simplicity.

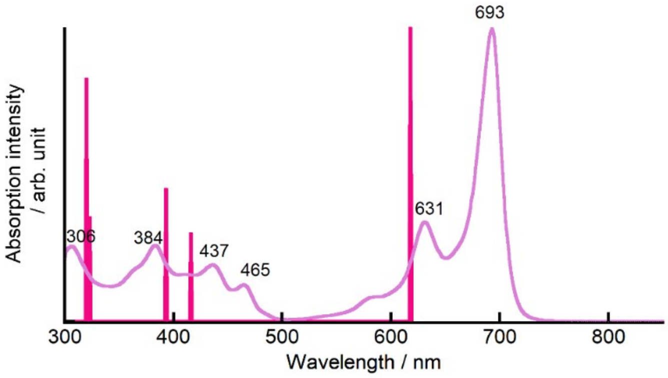

**Fig. S32.** Calculated absorption spectrum of **1** based on the TDDFT method at the B3LYP/6-31G(d) level (pink bars) overlaid on the UV/Vis absorption spectrum of **1** in chloroform.

**Table S6.** Summary of TDDFT calculation of **1** (B3LYP/6-31G(d)).

| $\lambda$ / nm | Oscillator strength | Major contributions |
|---|---|---|
| 618 | 0.5722 | H→L (100%) |
| 416 | 0.1704 | H–1→L (73%), H→L+2 (25%) |
| 393 | 0.2574 | H–1→L (22%), H→L+2 (74%) |
| 323 | 0.2024 | H–7→L (58%), H→L+4 (39%) |
| 320 | 0.4729 | H–7→L (39%), H→L+4 (54%) |

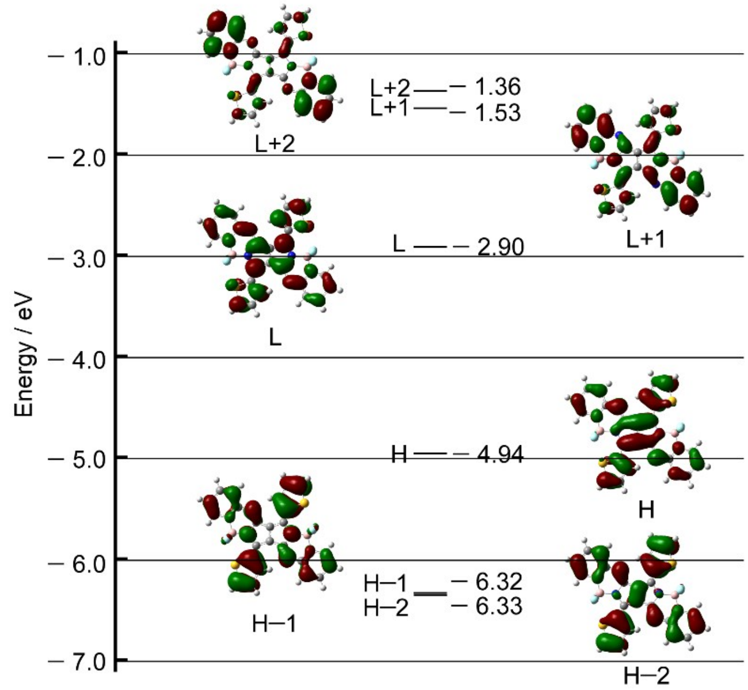

**Fig. S33.** Frontier molecular orbital diagrams of 1 from the HOMO–2 to LUMO+2 at the B3LYP/6-31G(d) level.

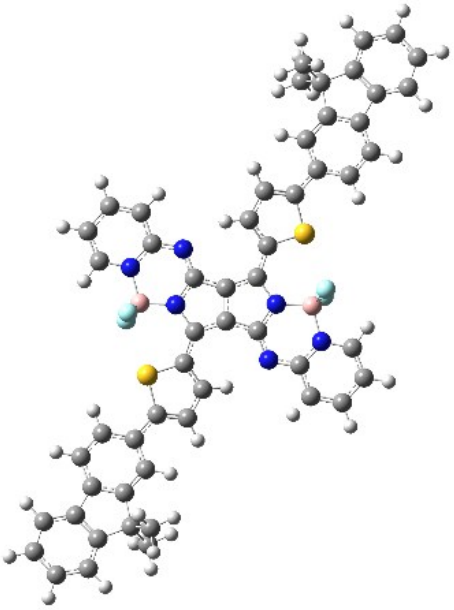

**Fig. S34.** An optimized structure of **5** at the B3LYP/6-31G(d) level. Alkoxy substituents were replaced with hydrogen atoms for simplicity.

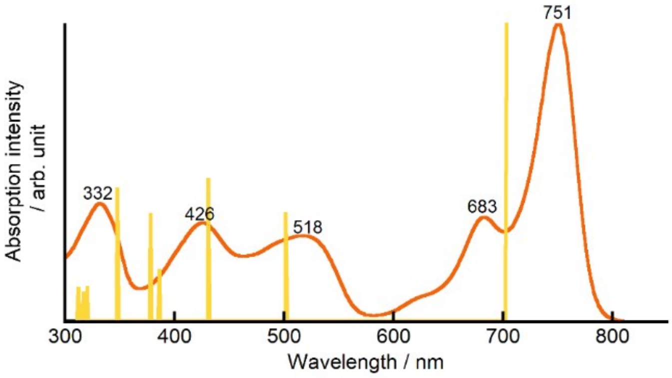

**Fig. S35.** Calculated absorption spectrum of **5** based on the TDDFT method at the B3LYP/6-31G(d) level (yellow bars) overlaid on the UV/Vis absorption spectrum of **5** in chloroform.

**Table S7.** Summary of TDDFT calculation of **5** (B3LYP/6-31G(d)).

| $\lambda$ / nm | Oscillator strength | Major contributions |
|---|---|---|
| 703 | 1.205 | H→L (100%) |
| 502 | 0.436 | H–2→L (94%) |
| 431 | 0.575 | H→L+2 (92%) |
| 386 | 0.204 | H–4→L (88%) |
| 378 | 0.432 | H→L+4 (91%) |
| 348 | 0.534 | H–1→L+1 (90%) |
| 320 | 0.135 | H–2→L+2 (75%), H→L+6 (19%) |
| 317 | 0.112 | H–2→L+2 (13%), H–1→L+3 (30%), H→L+6 (50%) |
| 312 | 0.132 | H–1→L+3 (65%), H→L+6 (19%) |

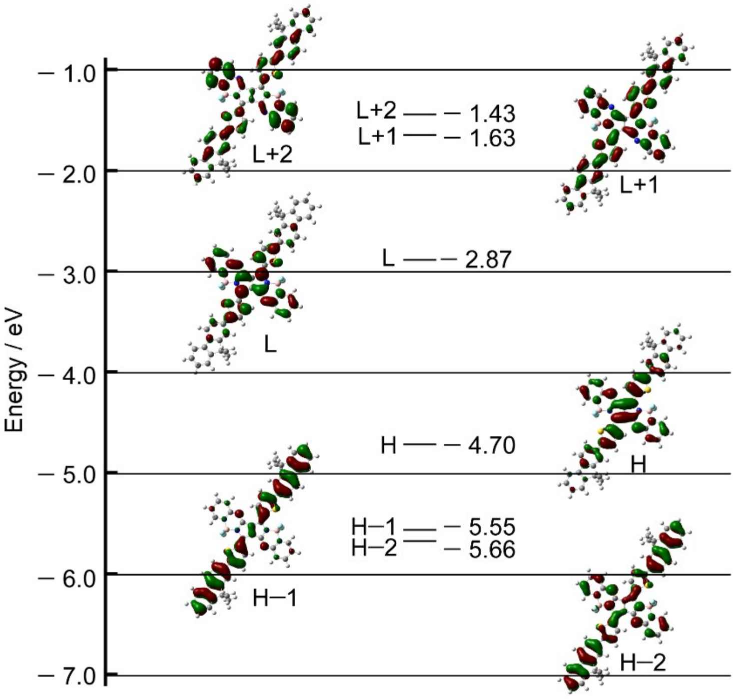

**Fig. S36.** Frontier molecular orbital diagrams of **5** from the HOMO–2 to LUMO+2 at the B3LYP/6-31G(d) level.

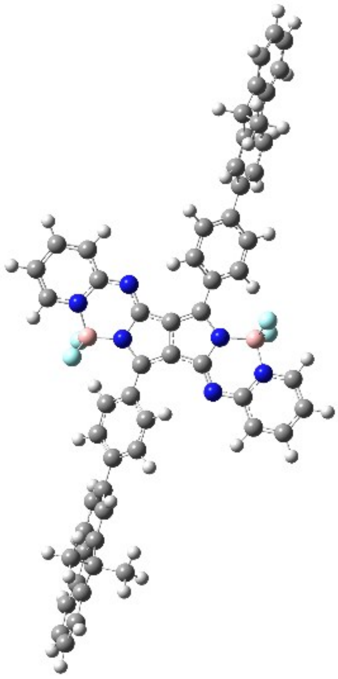

**Fig. S37.** An optimized structure of **10** at the B3LYP/6-31G(d) level. Alkoxy substituents were replaced with hydrogen atoms for simplicity.

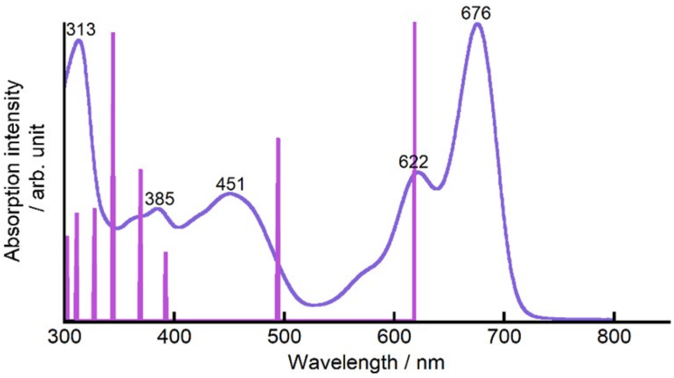

**Fig. S38.** Calculated absorption spectrum of **10** based on the TDDFT method at the B3LYP/6-31G(d) level (purple bars) overlaid on the UV/Vis absorption spectrum of **10** in chloroform.

**Table S8.** Summary of TDDFT calculation of **10** (B3LYP/6-31G(d)).

| $\lambda$ / nm | Oscillator strength | Major contributions |
|---|---|---|
| 619 | 0.820 | H→L (99%) |
| 494 | 0.500 | H–2→L (97%) |
| 392 | 0.187 | H→L+2 (94%) |
| 369 | 0.415 | H–6→L(13%), H–5→L (43%), H–4→L (34%) |
| 344 | 0.792 | H→L+4 (94%) |
| 327 | 0.307 | H–1→L+1 (95%) |
| 311 | 0.295 | H–2→L+2 (87%) |

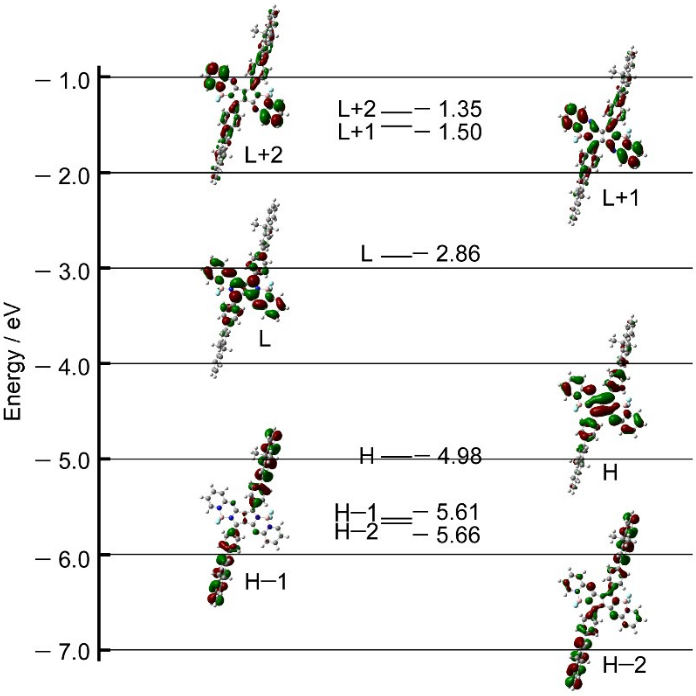

**Fig. S39.** Frontier molecular orbital diagrams of **10** from the HOMO–2 to LUMO+2 at the B3LYP/6-31G(d) level.

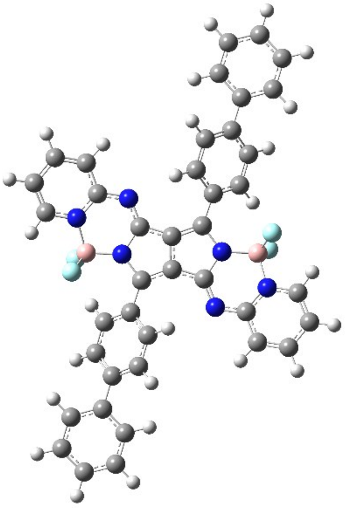

**Fig. S40.** An optimized structure of **11** based on DFT calculation at the B3LYP/6-31G(d) level. Alkoxy substituents were replaced by hydrogen atoms for simplicity.

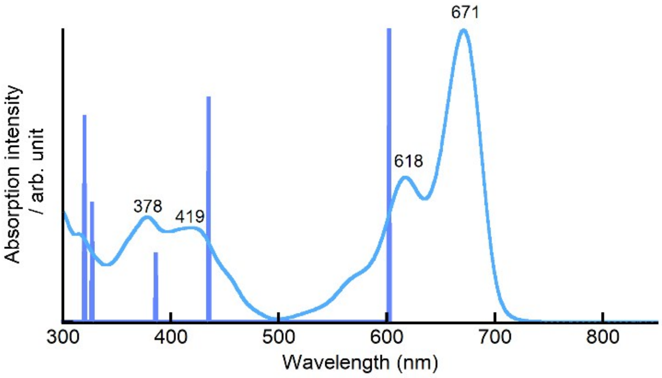

**Fig. S41.** Calculated absorption spectrum of **11** based on the TDDFT method at the B3LYP/6-31G(d) level (blue bars) overlaid on the UV/Vis absorption spectrum of **11** in chloroform.

**Table S9.** Summary of TDDFT calculation of **11** (B3LYP/6-31G(d)).

| $\lambda$ / nm | Oscillator strength | Major contributions |
|---|---|---|
| 602 | 0.6841 | H→L (100%) |
| 435 | 0.5247 | H–2→L (97%) |
| 386 | 0.159 | H→L+2 (98%) |
| 327 | 0.2786 | H–9-→L (25%), H→L+4 (72%) |
| 320 | 0.4805 | H–9→L (69%), H→L+4 (24%) |

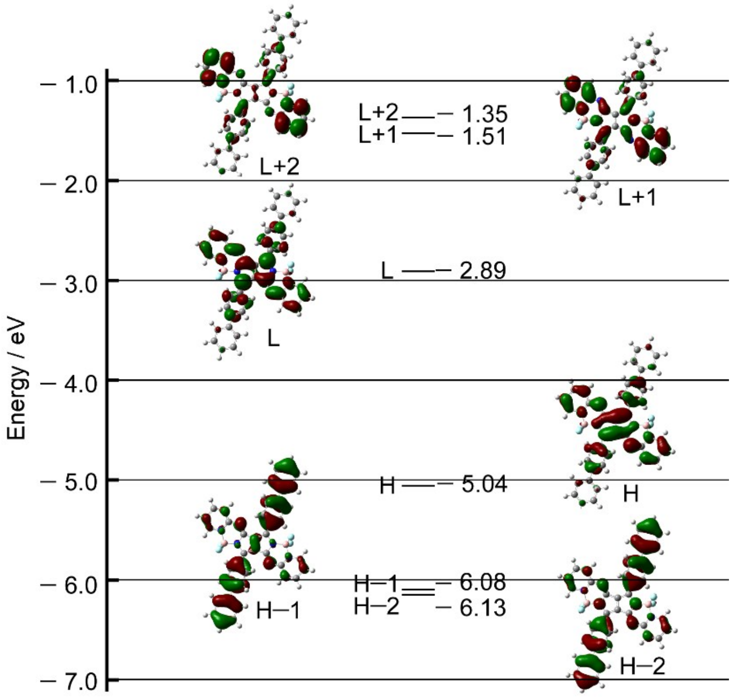

**Fig. S42.** Energies of molecular orbitals from the HOMO–2 to LUMO+2 of **11** based on DFT calculation at the B3LYP/6-31G(d) level.

## vi. Photovoltaic performance of dropcast films of 3/P3HT and 3/PC$_{71}$BM

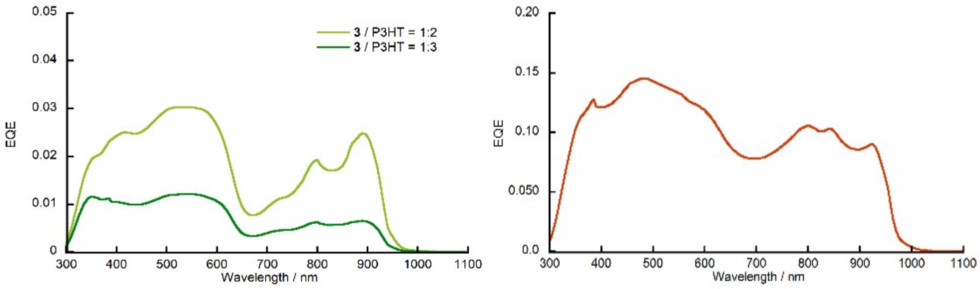

**Fig. S43.** EQE spectra of (left) the **3**/P3HT cells (1:3(w/w), pale green; 1:2(w/w), green) and (right) the **3** /PC$_{71}$BM cell (1:1(w/w)).

**Table S10.** Parameters of OPV cells.

| P | N | Ratio | Solvent | Additive | Active layer thickness / nm |
|---|---|---|---|---|---|
| P3HT | **3** | 1:2 | *o*-Dichlorobenzene | - | 63 |
| | | 1:3 | *o*-Dichlorobenzene | - | 69 |
| **3** | PC$_{71}$BM | 1:1 | Chloroform | 1,8-Diiodooctane | 207 |

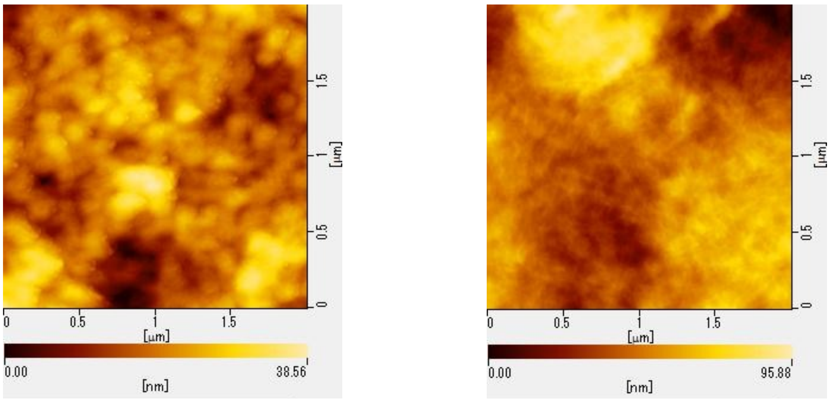

**Fig. S44.** AFM height images (2 × 2 μm) of (left) the **3**/P3HT cell (1:2(w/w)) and (right) the **3**/P3HT cell (1:3(w/w)).

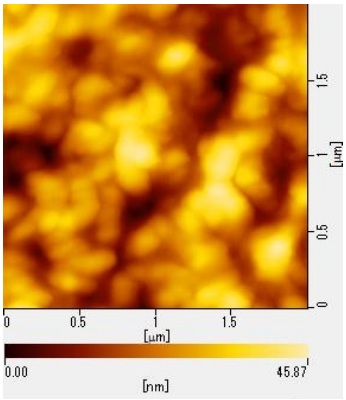

**Fig. S45.** AFM height image (2 × 2 μm) of the **3**/PC$_{71}$BM cell (1:1(w/w)).

## vii. References

1. Y. Wang, L. Chen, R. El-Shishtawy, S. Aziz and K. Müllen, *Chem.Commun.*, 2014, **50**, 11540.

2. M. Horn, Y. Hepuzer, Y. Yagci, B. Bilgin-Eran, U. Cernenco, V. Harabagiu, M. Pinteala and B. Simionescu, *Eur. Polym. J.*, 2002, **38**, 2197.

3. C. Morton, R. Gilmour, D. Smith, P. Lightfoot, A. Slawin and E. MacLean, *Tetrahedron*, 2002, **58**, 5547.