

Electronic Supplementary Information

Methyl Substituents Effect on Structure, Luminescent and Semiconducting Properties of Furan/Phenylene Co-oligomer Single Crystals

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1. Synthesis

Target compounds **4a**, **b** were synthesized according to previously described procedure (Scheme 1, Ref. 18 of the main text).

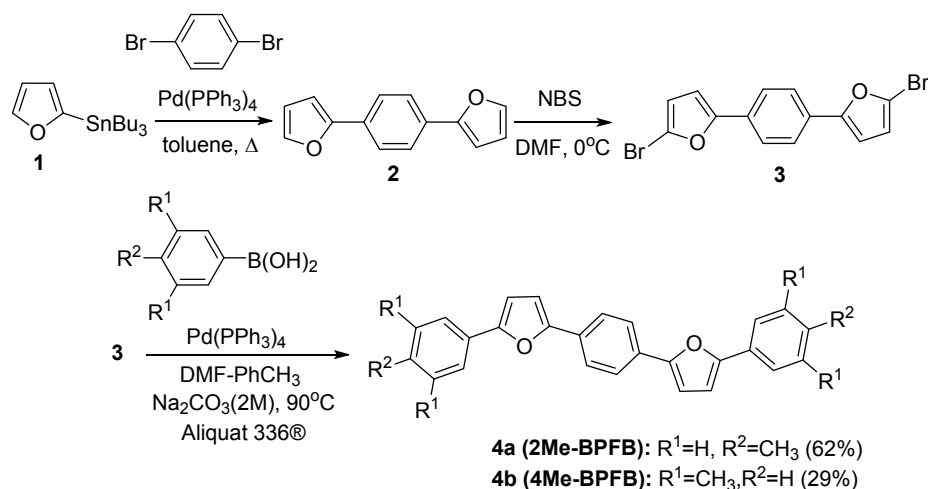


Figure S1. Synthesis of compounds **4a**, **b**.

Synthesis of 1,4-bis(5-(4-methylphenyl)furan-2-yl)benzene (**4a**, 2Me-BPFB).

A mixture of 1,4-bis(5-bromofuran-2-yl)benzene **3** (300 mg, 0.815 mmol), 4-methylphenylboronic acid (244 mg, 1.8 mmol), Pd(PPh₃)₄ (95 mg, 0.1 mmol), Na₂CO₃(2 M, 8 ml) and Aliquat 336® (0.1 ml) in DMF-PhCH₃ (1:1, 25 ml) was refluxed at 90°C for 36 h under Ar atmosphere. The precipitate formed was filtered, washed with water (3×10 ml), ethanol (3×10 ml) and hexane (3×10 ml). Vacuum sublimation at 300-310°C and 2·10⁻² torr gave yellow powder of **4a** (90 mg, 62%). mp 298-300°C; ¹H NMR (400 MHz, CDCl₃) δ): 7.74 (s, 4H, -C₆H₄-); 7.66 (d, *J*=8.1 Hz, 4H, -C₆H₄-Me); 7.23 (d, *J*=8.1 Hz, 4H, -C₆H₄-Me); 6.76 (d, *J*=3.4 Hz, 2H, FuH); 6.71 (d, *J*=3.4 Hz, 2H, FuH); 2.37 (s, 6H, CH₃); because of low solubility ¹³C NMR was not recorded; IR (KBr) 2914; 1500; 1479; 1117; 1024; 795 cm⁻¹; UV-vis (THF): λ_{max} = 379 nm; HRMS (ESI) *m/z*: calcd for C₂₈H₂₂O₂: 390.1614; found: 390.1617. Anal. calcd for C₂₈H₂₂O₂: C, 86.13; H, 5.68; found: C, 85.97; H, 5.55.

Synthesis of 1,4-bis(5-(3,5-dimethylphenyl)furan-2-yl)benzene (**4b**, 4Me-BPFB).

Compound **4b** was synthesized according to **4a** procedure from dibromide **3** (368 mg, 1 mmol) and (3,5-dimethylphenyl)boronic acid (330 mg, 2.2 mmol). Reaction time was 48 hr. Gradient sublimation at 310-320°C and 2·10⁻² torr gave yellow powder of **4b** (120 mg, 29%). mp 315-316°C; ¹H NMR (400 MHz, CDCl₃) δ): 7.78 (s, 4H, -C₆H₄-); 7.39 (s, 4H, -C₆H₃-Me₂); 6.93 (s, 2H, -C₆H₃-Me₂); 6.74 (dd, *J*=3.3 Hz, 4H, FuH); 2.38 (s, 12H, CH₃); because of low solubility ¹³C NMR was not recorded; IR (KBr) 2916; 1601; 1545; 1485; 1026; 798 cm⁻¹; UV-vis (THF): λ_{max} = 379 nm; HRMS (ESI) *m/z*: calcd for C₃₀H₂₆O₂: 418.1927; found: 418.1930. Anal. calcd for C₃₀H₂₆O₂: C, 86.09; H, 6.26; found: C, 86.40; H, 6.44.

2. Spectra of synthesized compounds

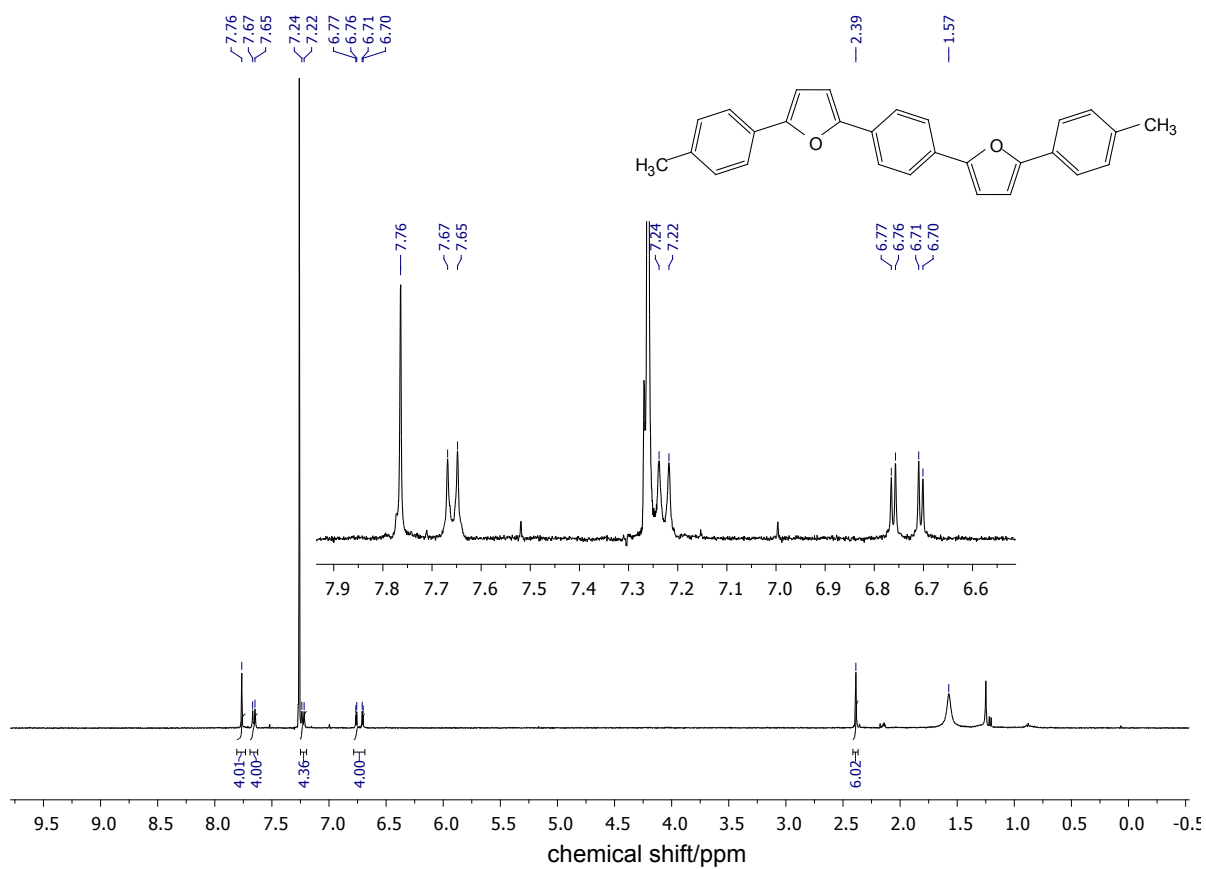


Figure S2. ¹H NMR spectrum of compound 4a in CDCl₃.

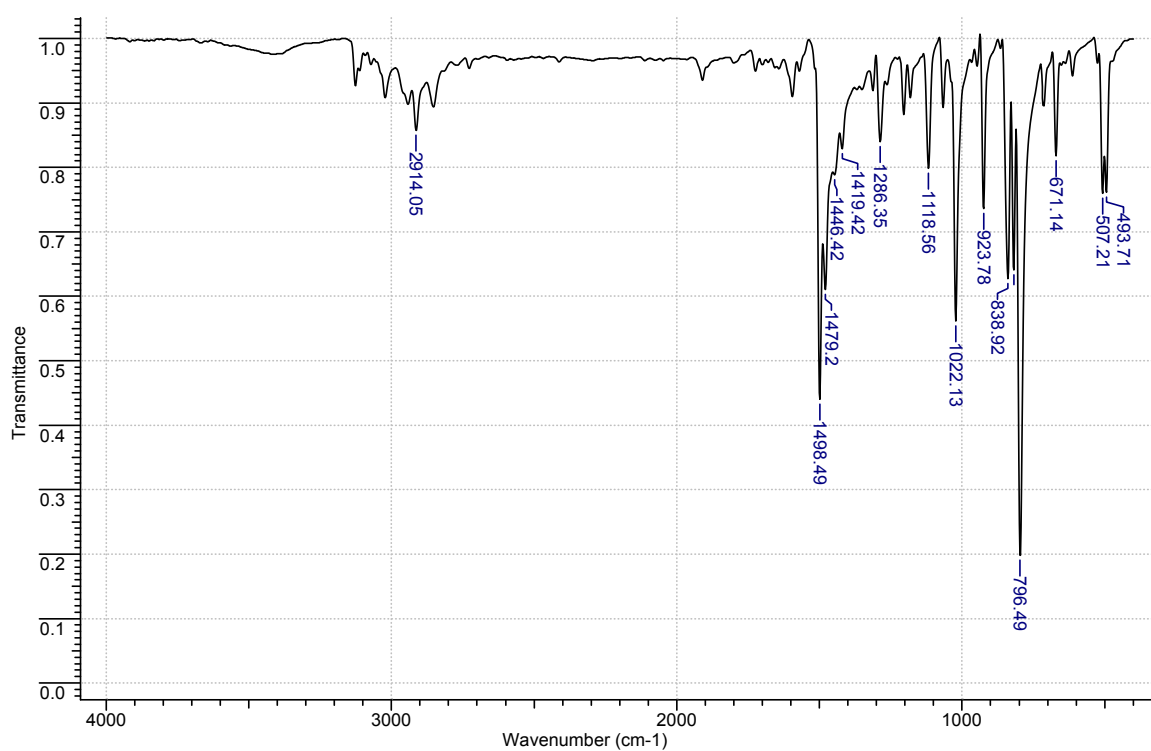


Figure S3. IR spectrum of **4a** in KBr.

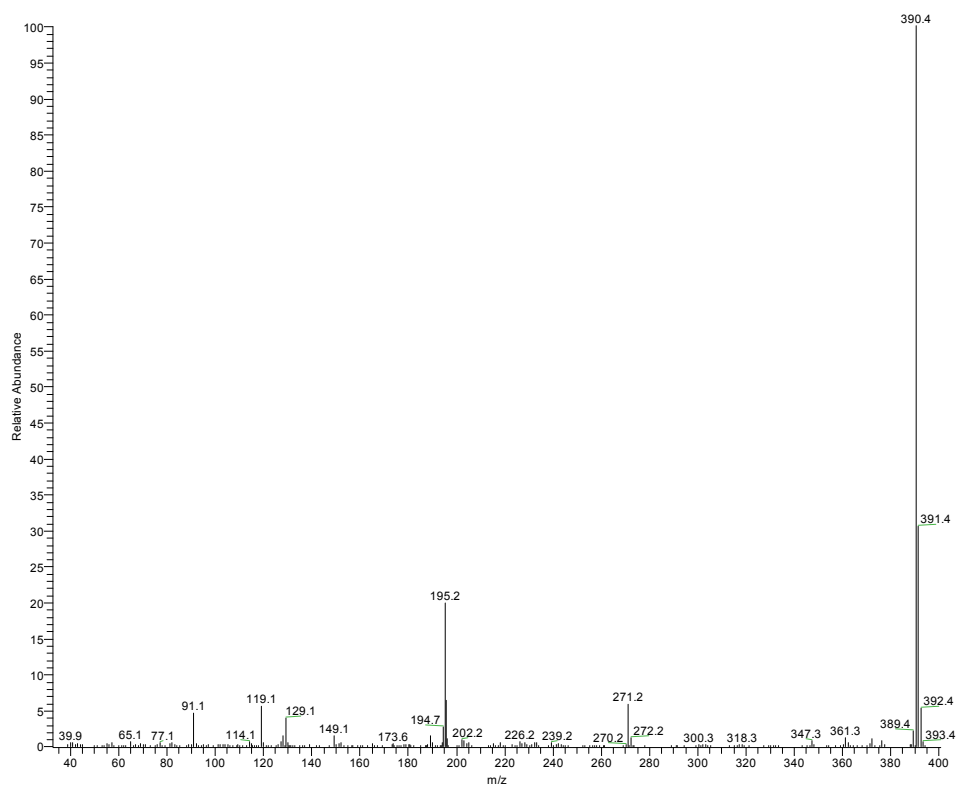


Figure S4. HRMS spectrum of compound **4a**.

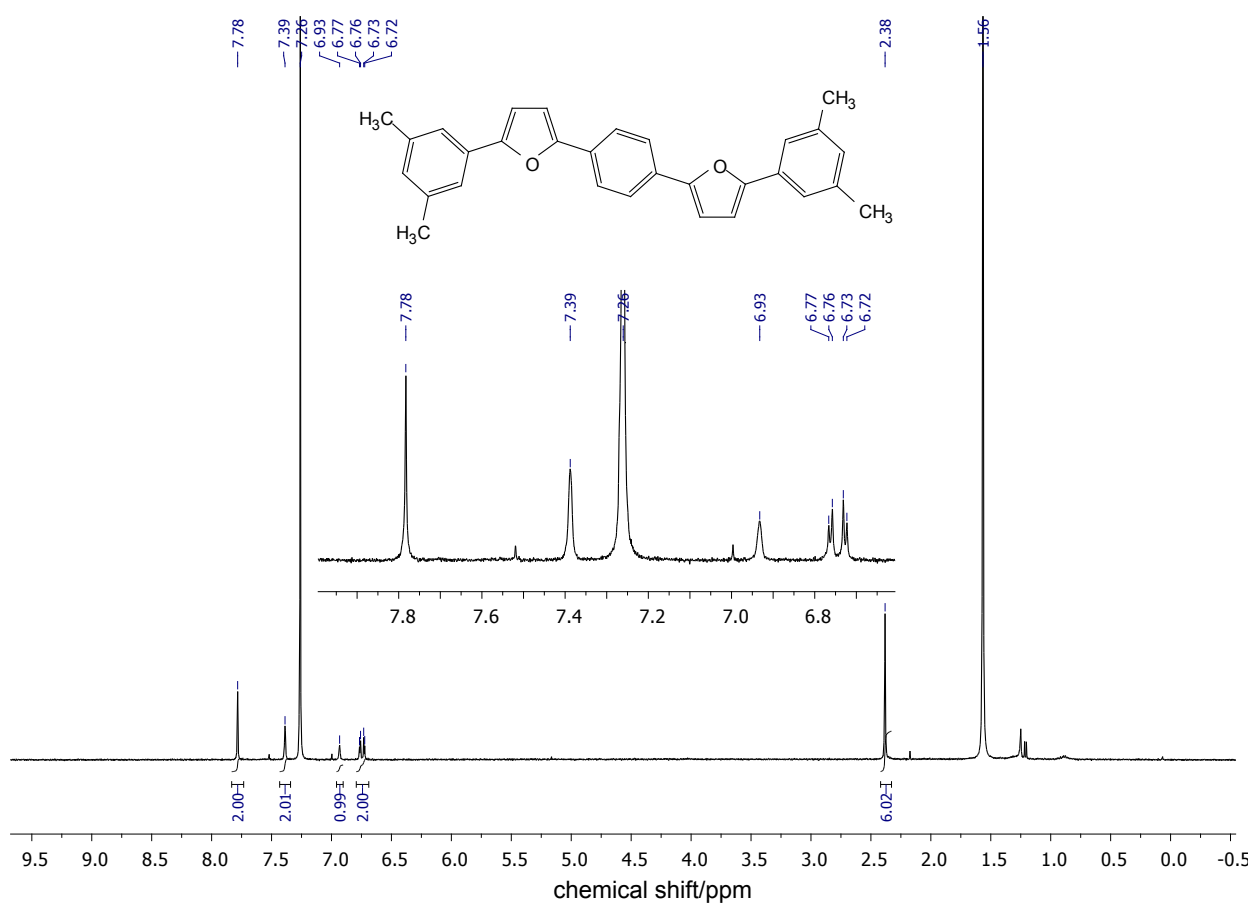


Figure S5. ¹H NMR spectrum of compound **4b** in CDCl₃.

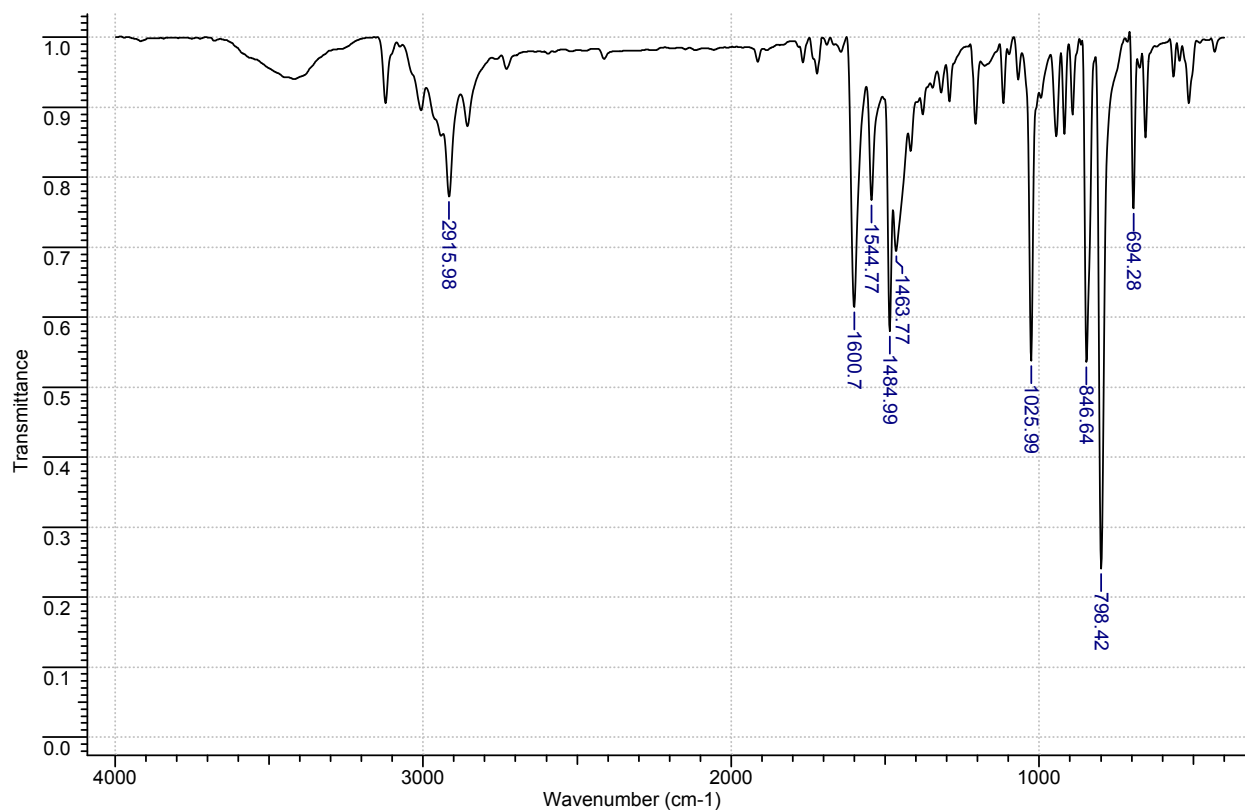


Figure S6. IR spectrum of **4b** in KBr.

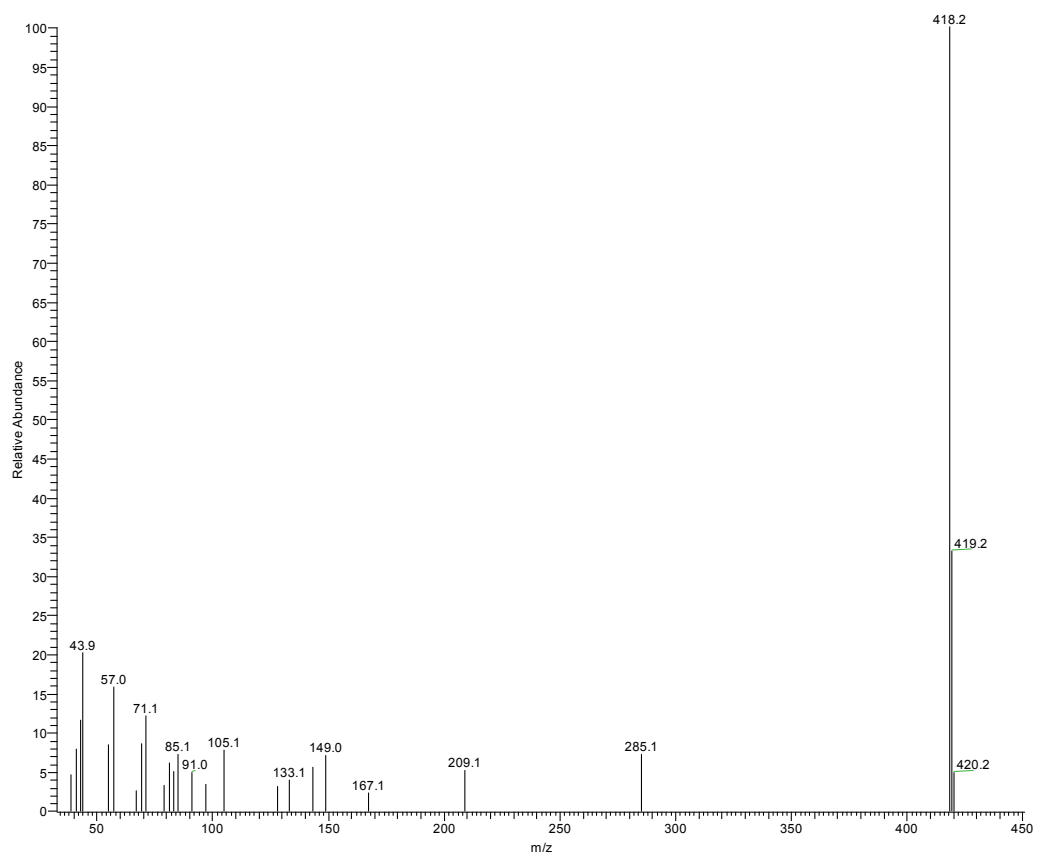


Figure S7. HRMS spectrum of compound **4b**.

3. Cyclic voltammetry and optical spectroscopy

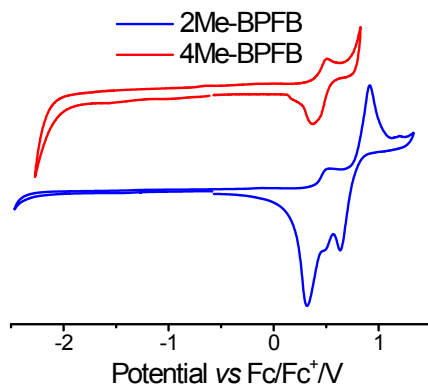
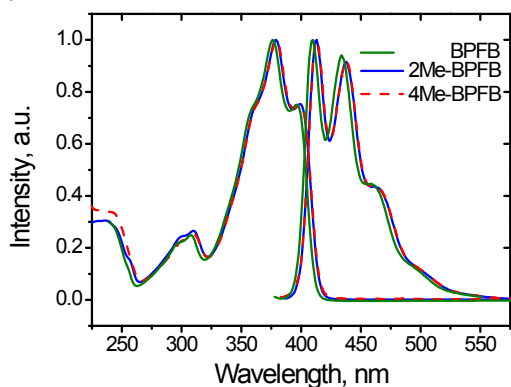
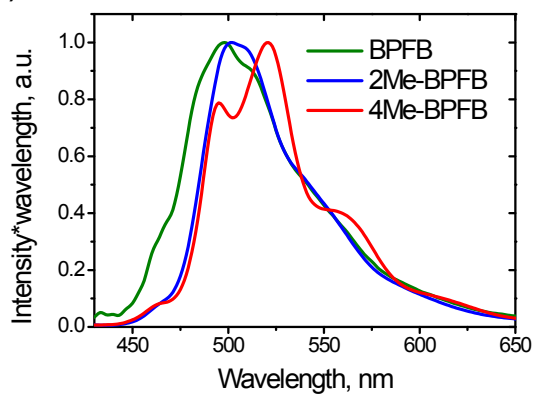


Figure S8. a) Cyclic voltammograms of 2Me-BPFB and 4Me-BPFB in CH_2Cl_2 .

a)



b)



c)

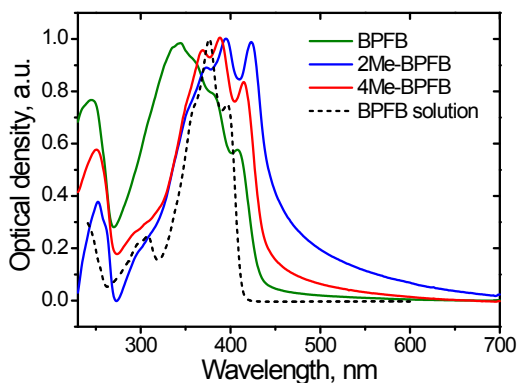


Figure S9. Optical spectra. a) Absorption and photoluminescence spectra of BPFB (solid olive lines), 2Me- (solid blue lines) and 4Me-BPFB (dashed red lines) in diluted THF solution; b) Photoluminescence spectra of BPFB (olive), 2Me- (blue) and 4Me-BPFB (red) single crystal; c) Optical density spectra of solid samples measured in potassium bromide pellets for BPFB (olive), 2Me-BPFB (blue) and 4Me-BPFB (red); the dark dashed line corresponds to BPFB absorption in THF solution. Note that the long-wavelength tails for the solid samples are mainly due to optical scattering from the grinded crystals.

4. Microscopy

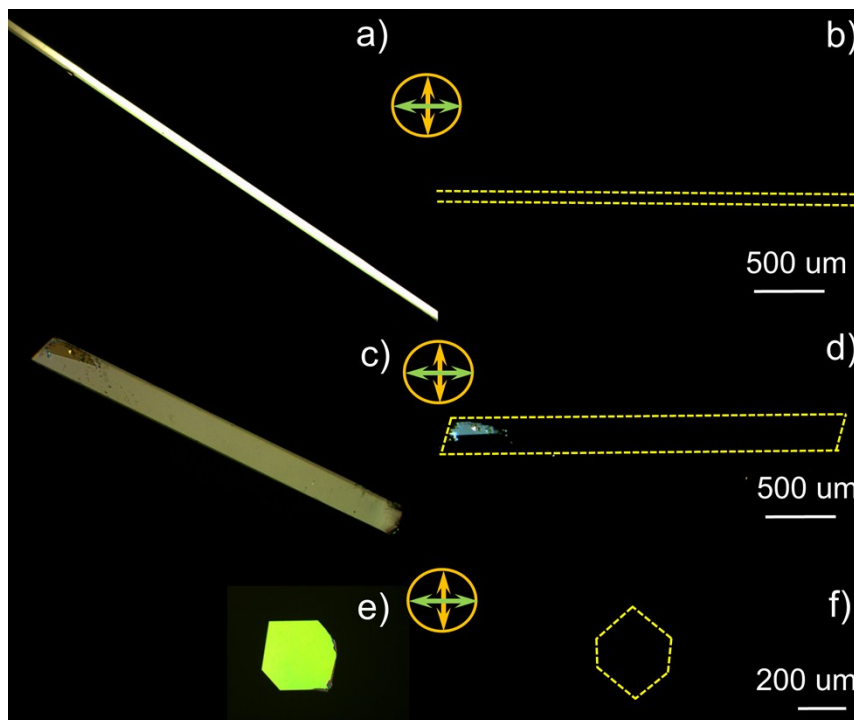


Figure S10. Optical images of the crystals in transmitted light through the crossed polarizers; a, b) 2Me-BPFB; c, d) 4Me-BPFB; e, f) BPFB; the arrows indicate the orientation of polarizer (orange) and analyzer (green).

5. X-ray study

The details of the X-ray diffraction data are as follows:

BPFB: light yellow rhombic plate, $(0.60 \times 0.56 \times 0.015)$ mm³, T 200(2) K, D_{calcd} 1.315 g·cm⁻³, $\mu(\text{Mo-K}\alpha)$ 0.082mm⁻¹, transmission 0.7869 - 0.9280, F(000) 380, (θ 1.01 – 25.00°, completeness 96.0%), 7983 measured reflections in index range $-24 \leq h \leq 23$, $-8 \leq k \leq 8$, $-7 \leq l \leq 7$, 1550 independent ($R_{\text{int}} = 0.0535$), 1115 observed ($I > 2\sigma(I)$), 127 parameters, $wR_2 = 0.1719$ (all data), GOOF 1.189, largest diff. peak and hole 0.218 and -0.307 e·Å⁻³. Note that the crystal structure for the vapor-grown BPFB single crystals was the same as the structure of previously reported solution-grown crystals (Ref. 18 of the main text).

2Me-BPFB: colorless prism, $(0.49 \times 0.22 \times 0.12)$ mm³, T 296(2) K, D_{calcd} 1.278 g·cm⁻³, $\mu(\text{Mo-K}\alpha)$ 0.079 mm⁻¹, transmission 0.834 - 0.862, F(000) 412, (θ 1.96 – 26.14°, completeness 99.8%), 24301 measured reflections in index range $-13 \leq h \leq 13$, $-7 \leq k \leq 7$, $-19 \leq l \leq 19$, 2021 independent ($R_{\text{int}} = 0.0413$), 1755 observed ($I > 2\sigma(I)$), 137 parameters, $wR_2 = 0.1258$ (all data), GOOF 1.157, largest diff. peak and hole 0.187 and -0.216 e·Å⁻³. Hydrogen positions of methyl groups in 2Me-BPFB were disordered in the ratio 75:25.

4Me-BPFB: yellow needle, (0.95 × 0.40 × 0.06) mm³, T 296(2) K, D_{calcd} 1.245 g·cm⁻³, $\mu(\text{Mo-K}\alpha)$ 0.076mm⁻¹, transmission 0.8069 - 0.8620, F(000) 444, (θ 1.54 – 25.11°, completeness 99.6%), 13206 measured reflections in index range $-15 \leq h \leq 15$, $-6 \leq k \leq 6$, $-18 \leq l \leq 18$, 1995 independent (R_{int} 0.0376), 1755 observed ($I > 2\sigma(I)$), 147 parameters, wR_2 0.1815 (all data), GOOF 1.233, largest diff. peak and hole 0.293 and - 0.415 e.Å⁻³. Hydrogen positions of methyl groups in 4Me-BPFB were disordered in the ratios: 55:45 for C14- and 62:38 for C15-methyl groups.

Table S1. Selected crystallographic and structural data; φ_1 and φ_2 are the twisting angles between furan and phenyl rings (Figure 4a, main text). d_{max} is the maximal deviation of atom C10 from the average plane of π -system.

Compound	BPFB	2Me-BPFB	4Me-BPFB
Empirical formula	C ₂₆ H ₁₈ O ₂	C ₂₈ H ₂₂ O ₂	C ₃₀ H ₂₆ O ₂
Crystal system	monoclinic		
Space group	$P2_1/c$		
a , Å	20.407(4)	11.0733(7)	13.2404(6),
b , Å	7.300(1)	6.1594(3)	5.4901(2)
c , Å	6.200(1)	15.850(1)	15.3541(7)
β , °	97.773(6)	110.183(2)	90.015(2)
V , Å ³	915.1(3)	1014.7(1)	1116.11(8)
Z	2		
final R_1 for ($I > 2\sigma(I)$)	0.0567	0.0355	0.0494
density, g·cm ⁻³	1.315	1.278	1.245
tilt angle	87.8	28.2	36.3
φ_1	15.3	12.7	19.3
φ_2	-13.1	-9.4	-8.8
d_{max} , Å	±0.3975	±0.3947	±0.4418
herringbone angle, ^a °	35.8	35.4	57.1
intradimer distance, ^b Å	4.786	6.159	5.490
stacking angle, ^c °	-	18.5	36.6

^ameasured between the average planes of π -systems; ^bthe distance between the centers of central phenyl rings of the nearest neighboring molecules, this distance was found to correspond to b-axis for 2Me- and 4Me-BPFB; ^cthe angle between the average plane of π -system and the charge transport direction (b-axis).

Table S2. Intermolecular C-H... π interactions in crystals of BPFB, 2Me-BPFB and 4Me-BPFB. C_g is the aromatic ring center; D_{pln} is the nearest distance between H-atom and aromatic ring plane; Cycle1 is the furan ring; Cycle2 is the terminal phenyl ring; Cycle2* is the terminal phenyl ring belonging to the neighboring layer; Cycle3 is the central phenyl ring (Figure 4 in the main text).

Compound	Interaction	H...C _g , (Å)	D _{pln} , (Å)	C-H...C _g , (°)
BPFB	C2-H... π (Cycle2)	2.77	2.75	137
	C8-H... π (Cycle3)	2.82	2.79	136
	C11-H... π (Cycle2)	2.84	2.82	138
2Me-BPFB	C2-H... π (Cycle2*)	2.84	2.82	138
	C8-H... π (Cycle2)	2.93	2.87	127
	C11-H... π (Cycle3)	2.99	2.94	141
4Me-BPFB	C13-H... π (Cycle1)	2.79	2.79	130
	C15-H... π (Cycle1)	2.87	2.74	151
	C14-H... π Cycle2)	2.87	2.71	177

6. OFET data

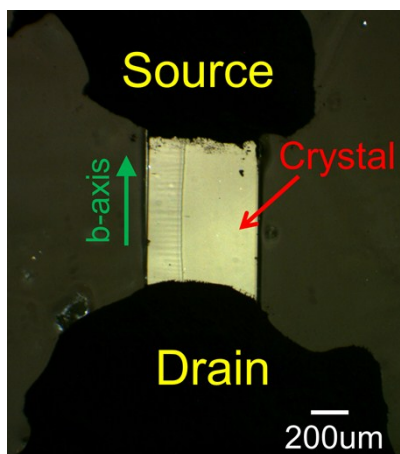


Figure S11. Optical image of 4Me-BPFB single crystal with painted source-drain contacts.

Table S3. Parameters of fabricated single-crystal OFETs. W , L are channel width and length respectively; d and C are the thickness and capacitance of the dielectric layer, correspondingly.

Crystal type	Sample №	W [mm]	L [mm]	W/L	μ [cm ² /Vs]	V_{th} [V]
BPFB	1	0.95	0.49	1.94	0.065	-19
	2	2.60	0.78	3.33	0.13	-10
	3	1.36	0.61	2.23	0.13	-16
				average:	0.11±0.04	-15±4
4Me-BPFB	1	0.58	0.77	0.75	0.039	-8
	2	1.36	0.85	1.60	0.038	-14
	3	0.23	0.44	0.52	0.040	-20
				average:	0.039±0.001	-14±6