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Supplementary Information

Quantitative Evaluation of Photoinduced Bending Speed of Diarylethene Crystals

Daichi Kitagawa [1], Chika Iwaihara [1], Hiroyasu Nishi [1,2] and Seiya Kobatake [1,*]

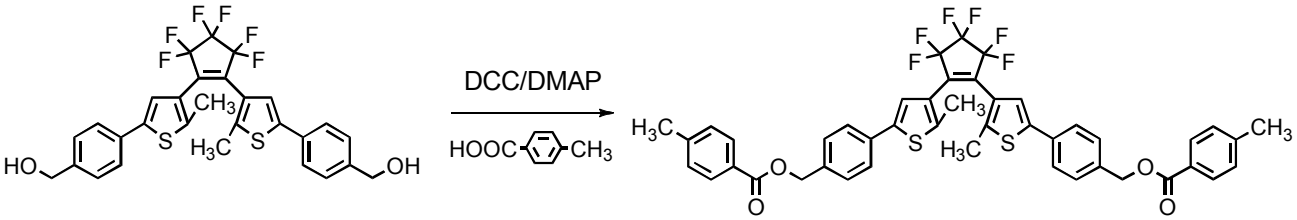
[1] Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan; E-Mail: kitagawa@bioa.eng.osaka-cu.ac.jp

[2] Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan; E-Mail: nishi-h@iis.u-tokyo.ac.jp

* Author to whom correspondence should be addressed; E-Mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Tel./Fax: +81-6-6605-2797.

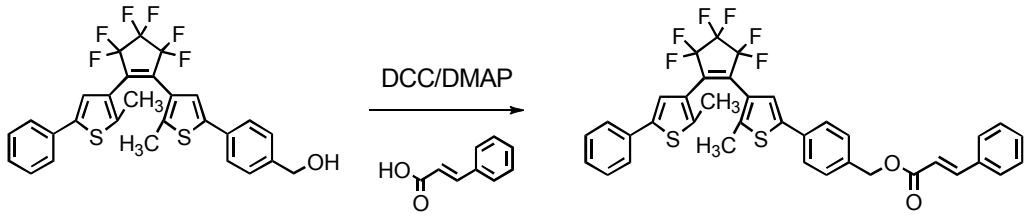
Materials

1,2-Bis(2-methyl-5-(4-(*p*-toluyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene (2)



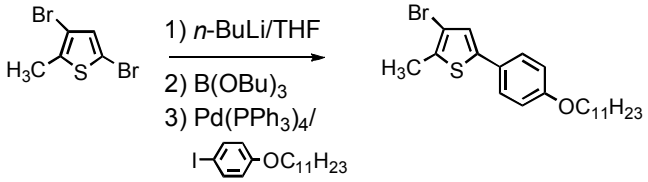
A solution of 1,2-bis(2-methyl-5-(4-hydroxymethylphenyl)-3-thienyl)perfluorocyclopentene [1] (300 mg; 0.52 mmol), *p*-toluic acid (140 mg; 1.0 mmol), dicyclohexylcarbodiimide (469 mg; 2.3 mmol), *N*,*N*-dimethyl-4-aminopyridine (140 mg; 1.1 mmol), and anhydrous tetrahydrofuran (THF) (20 mL) was stirred overnight under argon atmosphere at room temperature. The reaction mixture was treated with an aqueous solution of sodium hydrogen carbonate, and the mixture was extracted with ether. The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica-gel using *n*-hexane/ethyl acetate (7:3) as the eluent. Pure **2** was obtained by a further purification with high-performance liquid chromatography (HPLC) and recrystallization from *n*-hexane/ether solution. Yield: 290 mg (69%). **2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 5.35 (s, 4H, CH_2), 7.24 (d, J = 8.2 Hz, 4H, Ar), 7.28 (s, 2H, Ar), 7.46 (d, J = 8.3 Hz, 4H, Ar), 7.55 (d, J = 8.3 Hz, 4H, Ar), 7.96 (d, J = 8.2 Hz, 4H, Ar). HR-MS (FAB) *m/z* = 816.1797 (M^+); Calcd. for $C_{45}H_{34}F_6O_4S_2$: 816.1803. Single crystal of **2** was obtained by recrystallization from *n*-hexane.

1-(2-Methyl-5-(4-(cinnamoyloxymethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene (4)



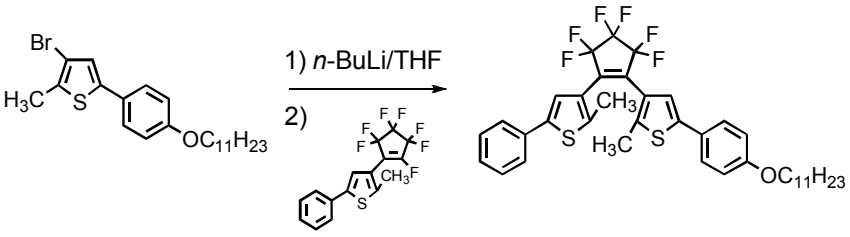
A solution of 1-[2-methyl-5-(4-hydroxymethylphenyl)-3-thienyl]-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [2] (600 mg; 1.0 mmol), cinnamic acid (323 mg; 2.2 mmol), dicyclohexylcarbodiimide (495 mg; 2.4 mmol), *N*,*N*-dimethyl-4-aminopyridine (147 mg; 1.2 mmol), and anhydrous THF (25 mL) was stirred overnight under argon atmosphere at room temperature. The reaction mixture was treated with an aqueous solution of sodium hydrogen carbonate, and the mixture was extracted with ether. The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica-gel using *n*-hexane/ethyl acetate (7:3) as the eluent. Pure **4** was obtained by a further purification with recrystallization from *n*-hexane. Yield: 605 mg (82%). **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 6.49 (d, *J* = 16.0 Hz, 1H, CH), 7.28–7.57 (m, 16H, Ar), 7.74 (d, *J* = 16.0 Hz, 1H, CH). HR-MS (FAB) *m/z* = 680.1272 (M^+); Calcd. for $C_{37}H_{26}F_6O_2S_2$: 680.1278.

3-Bromo-2-methyl-5-(4-undecyloxyphenyl)thiophene



To 40 mL of dry THF containing 3,5-dibromo-2-methylthiophene (3.0 g; 12 mmol) was added 9.0 mL of 1.6 M *n*-BuLi hexane solution (14 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at the low temperature. Tri-*n*-butyl borate (4.0 mL; 15 mmol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 1 h at that temperature. The reaction mixture was quenched with water. To the residue were added 20 wt % Na_2CO_3(aq) (13 mL), 1-iodo-4-undecyloxybenzene (4.4 g; 12 mmol), and $Pd(PPh_3)_4$ (0.35 g; 0.30 mmol). After the mixture was refluxed for 14 h at 70 °C, it was neutralized by HCl(aq) and extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by silica-gel column chromatography using *n*-hexane as the eluent to give 2.6 g of the product in 73% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.7 Hz, 3H), 1.2–1.5 (m, 16H), 1.7–1.9 (m, 2H), 2.40 (s, 3H), 3.96 (t, *J* = 6.5 Hz, 2H), 6.88 (d, *J* = 8.8, 2H), 6.98 (s, 1H), 7.41 (d, *J* = 8.8, 2H).

1-(2-Methyl-5-(4-(undecyloxy)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (5)



To 20 mL of dry THF solution containing 3-bromo-2-methyl-5-(4-undecyloxyphenyl)thiophene (0.50 g, 1.2 mmol) was added 0.9 mL of 1.6 M *n*-BuLi hexane solution (14 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at the low temperature. 1-(2-Methyl-5-phenyl-3-thienyl)heptafluorocyclopentene [2] (0.51 g; 1.4 mmol) in dry THF (5.0 mL) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 1 h at that temperature. The reaction mixture was quenched with water and extracted with ether. The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica-gel using *n*-hexane/dichloromethane (9:1) as the eluent. Pure **5** was obtained by a further purification with HPLC. Yield: 230 mg (29%). Single crystal **5** was obtained by recrystallization from methanol. **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.89 (t, *J* = 6.7 Hz, 3H), 1.2–1.5 (m, 16H), 1.7–1.9 (m, 2H), 1.95 (s, 3H), 1.97 (s, 3H), 3.98 (t, *J* = 6.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.15 (s, 1H), 7.28 (s, 1H), 7.26–7.42 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H). HR-MS (FAB) *m*/*z* = 690.2424 (M^+); Calcd. for $C_{38}H_{40}F_6OS_2$: 690.2425.

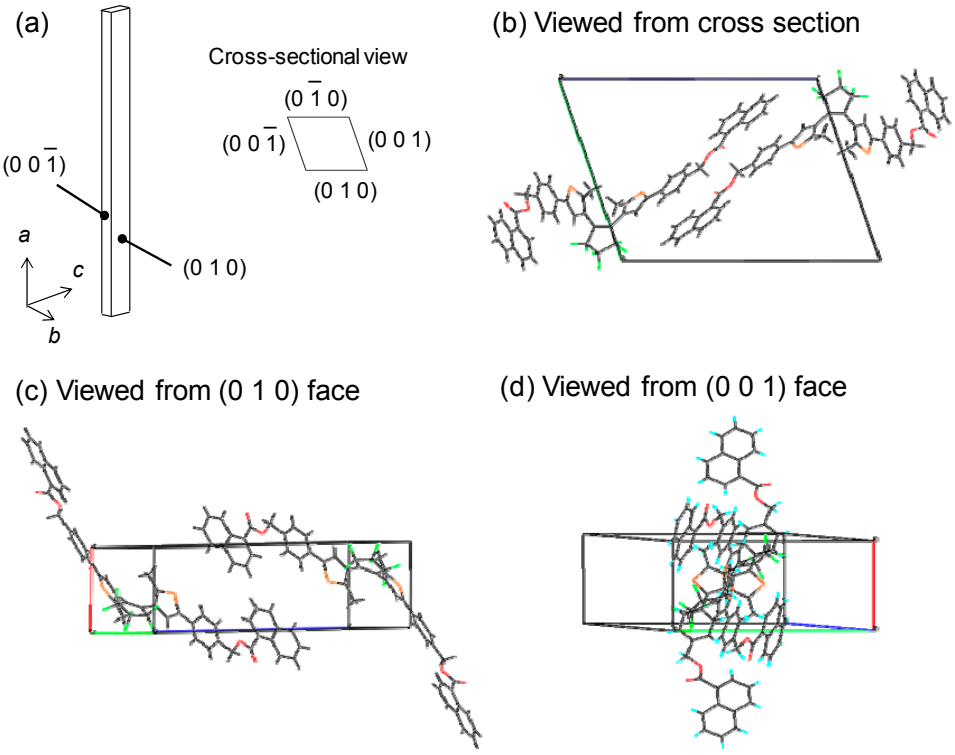


Figure S1. (**a**) Crystal shape of **1** and molecular packing diagrams viewed from (**b**) cross section, (**c**) (0 1 0) face, and (**d**) (0 0 1) face.

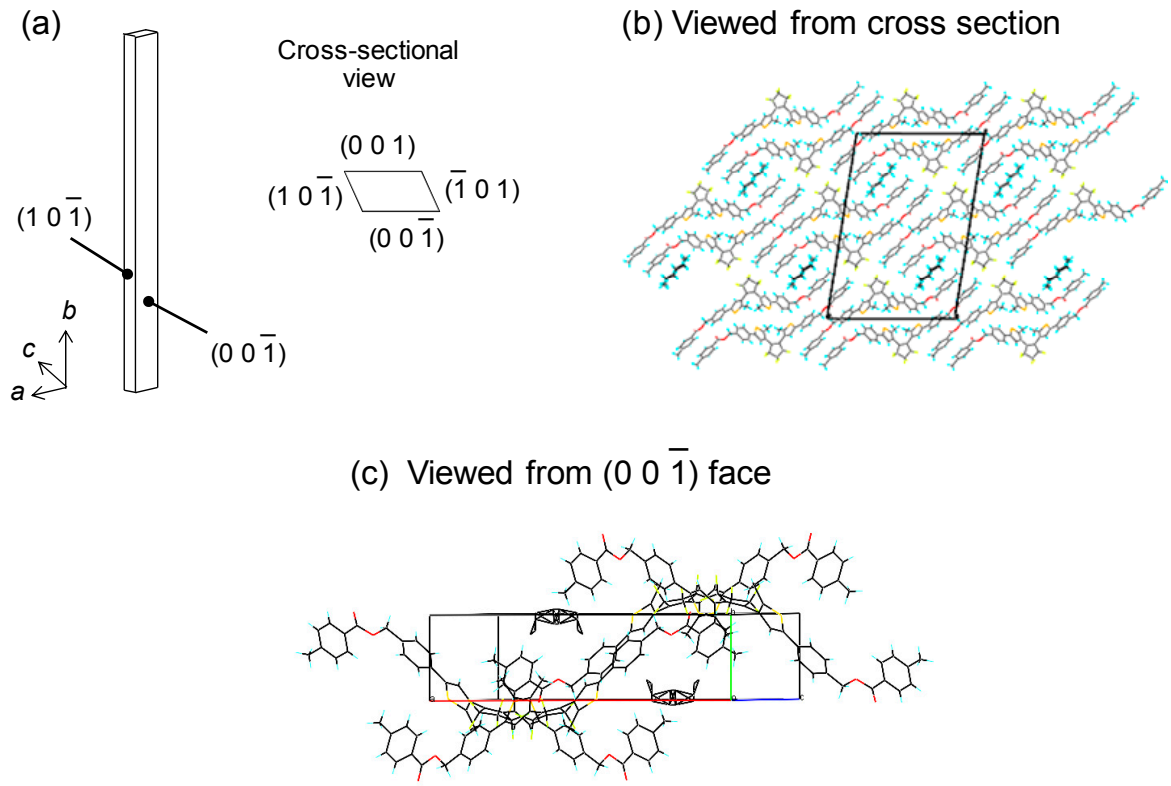


Figure S2. (**a**) Crystal shape of **2** and molecular packing diagrams viewed from (**b**) cross section and (**c**) (0 0 $\bar{1}$) face.

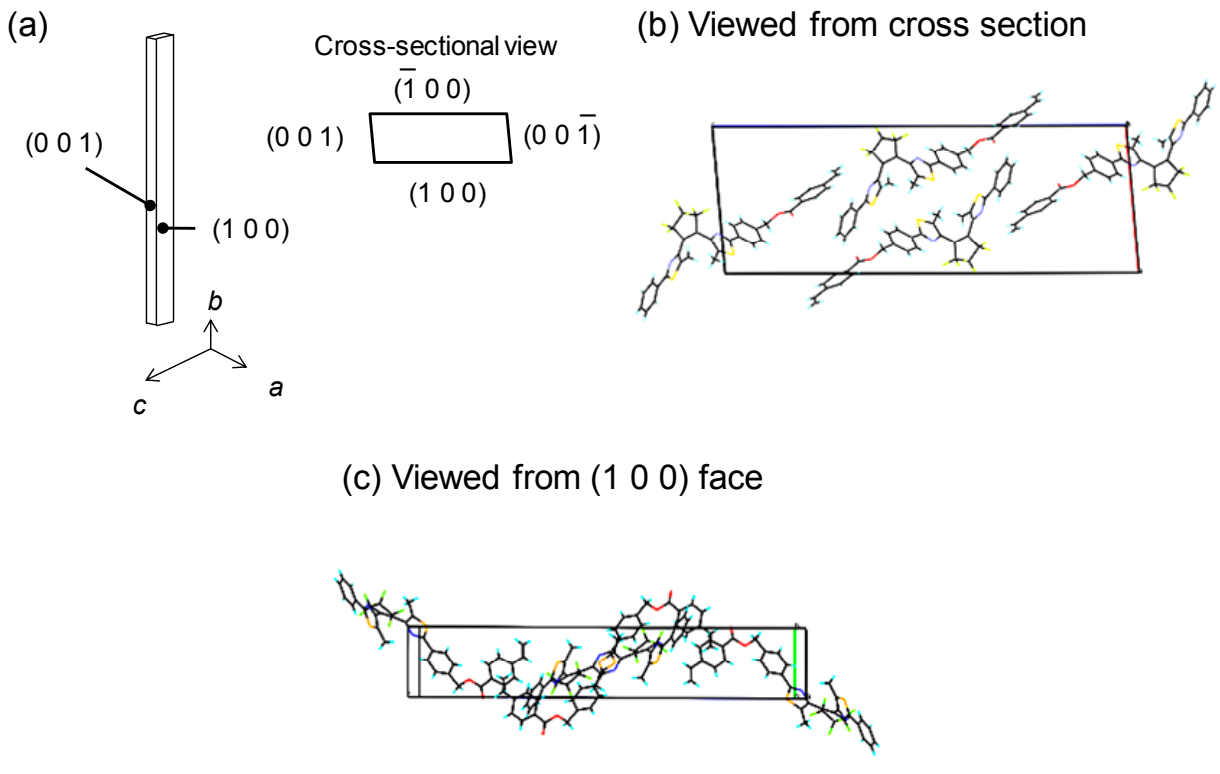


Figure S3. (**a**) Crystal shape of **3** and molecular packing diagrams viewed from (**b**) cross section and (**c**) (1 0 0) face.

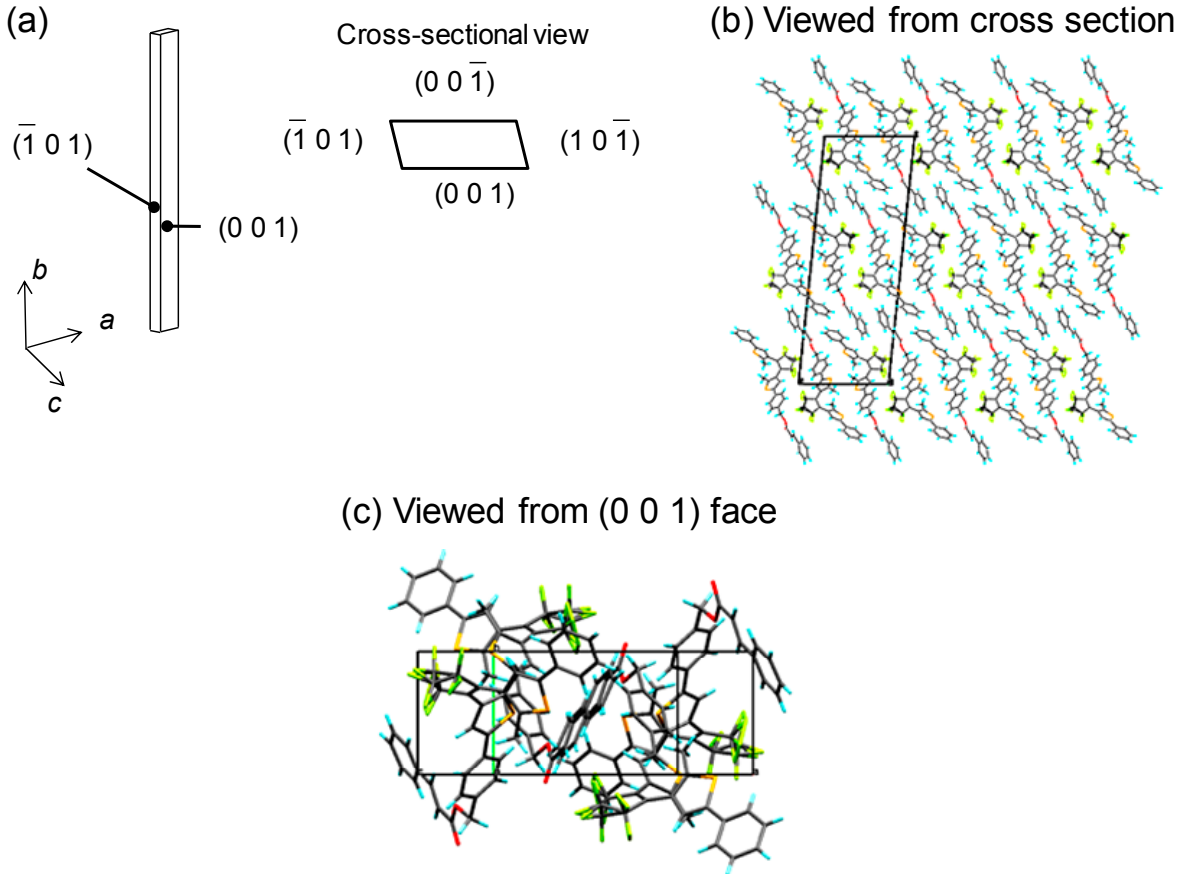


Figure S4. (**a**) Crystal shape of **4** and molecular packing diagrams viewed from (**b**) cross section and (**c**) (0 0 1) face.

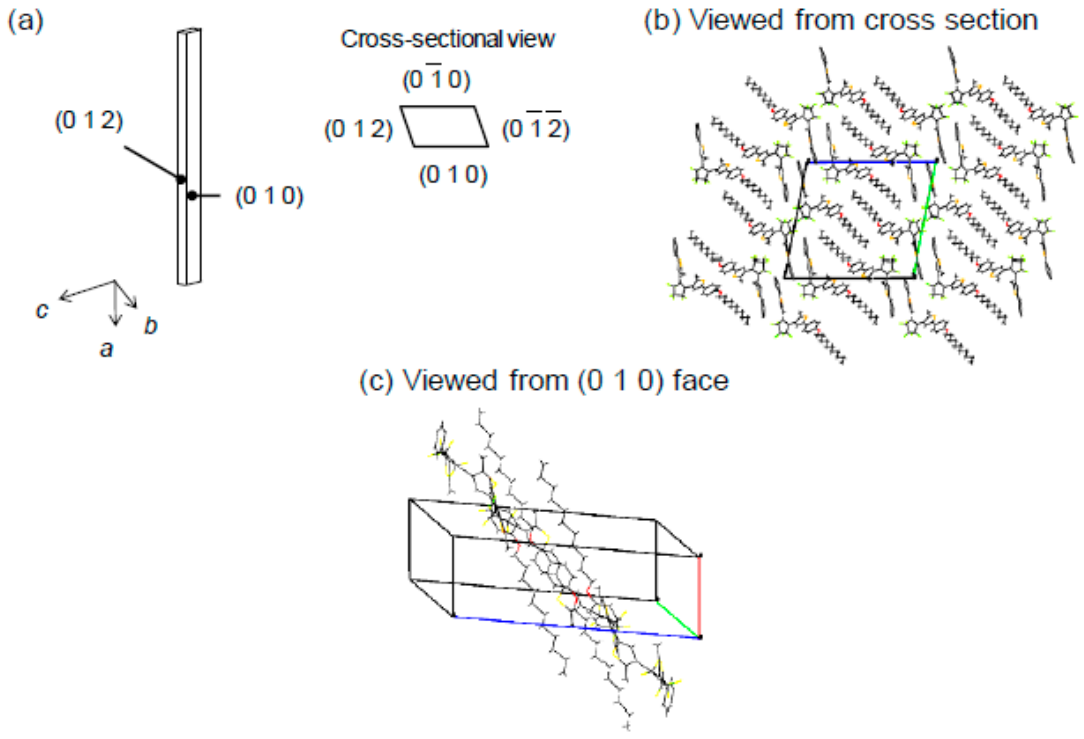


Figure S5. (**a**) Crystal shape of **5** and molecular packing diagrams viewed from (**b**) cross section and (**c**) (0 1 0) face.

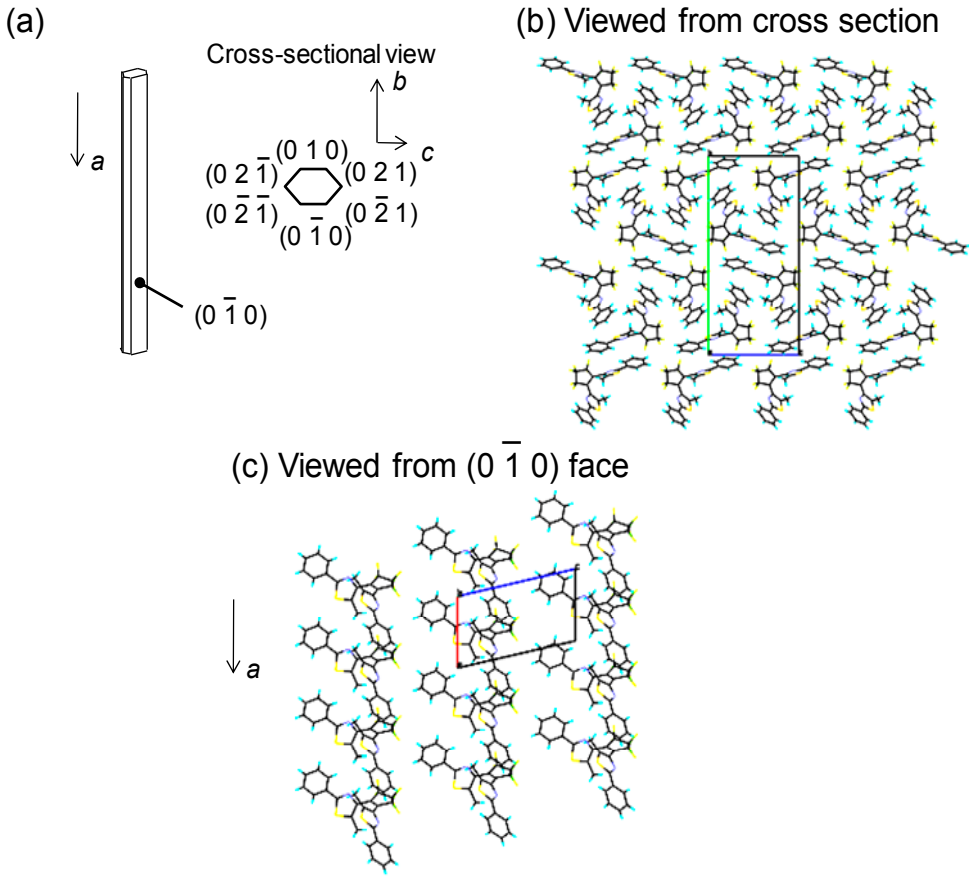


Figure S6. (**a**) Crystal shape of **6** and molecular packing diagrams viewed from (**b**) cross section and (**c**) (0 $\bar{1}$ 0) face.

Table S1. Crystal data for diarylethenes **1**−**6.**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{51}H_{34}F_6O_4S_2$	$C_{48}H_{41}F_6O_4S_2$	$C_{35}H_{24}F_6N_2O_2S_2$	$C_{37}H_{26}F_6O_2S_2$	$C_{38}H_{40}F_6OS_2$	$C_{25}H_{16}F_6N_2S_2$
Formula weight	888.92	859.93	682.70	680.70	690.82	522.53
Temperature/K	138(2)	120(2)	138(2)	153(2)	138(2)	123(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	6.838(2)	21.493(10)	12.979(2)	13.335(8)	7.5493(9)	7.236(2)
b/Å	15.416(6)	6.174(3)	6.620(1)	6.335(4)	20.955(3)	25.752(8)
c/Å	20.719(8)	32.059(15)	36.186(5)	37.131(18)	22.977(3)	12.611(4)
α/°	70.74(3)	90	90	90	77.918(3)	90
β/°	88.28(3)	98.765(6)	94.888(3)	95.97(4)	84.857(4)	102.432(5)
γ/°	89.84(3)	90	90	90	80.747(3)	90
Volume/Å^3	2060.9(13)	4205(3)	3097.7(8)	3120(3)	3502.1(7)	2295.0(12)
Z	2	4	4	4	4	4
Density/g·cm^{-3}	1.432	1.358	1.464	1.449	1.310	1.512
Goodness-of-fit on F^2	1.046	1.080	1.029	1.037	0.953	0.989
$R(I > 2\sigma(I))$	$R1 = 0.0442$	$R1 = 0.0564$	$R1 = 0.0559$	$R1 = 0.0553$	$R1 = 0.0708$	$R1 = 0.0575$
R(all data)	$wR2 = 0.0912$	$wR2 = 0.1334$	$wR2 = 0.1695$	$wR2 = 0.1481$	$wR2 = 0.2079$	$wR2 = 0.1530$
CCDC No.	942519 [3]	1420116	973009 [4]	1420111	1420171	282860 [5]

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