<u>Supporting Information:</u>

Photoinduced rapid and explosive fragmentation of diarylethene crystals having urethane bonding

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Movie S1. Photoinduced rapid and explosive fragmentation of crystal **1a**. The movie was taken in the real time.

Movie S2. Photoinduced rapid and explosive fragmentation of crystal **2a**. The movie was taken in the real time.

Experimental Section

    General. Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane as the internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700/700S mass spectrometer. UV−vis absorption spectra were measured with a JASCO V-560 absorption spectrometer. Photoirradiation in solution was conducted using a 200 W mercury−xenon lamp (Moritex MUV-202) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV) and glass filters. Photoinduced fragmentation of diarylethene crystals was observed using a Keyence VHX-500 digital microscope. Single crystal X-ray crystallographic analysis was carried out using a Rigaku RAXIS RAPID imaging plate diffractometer or a Rigaku AFC/Mercury CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97. UV irradiation was carried out using a Keyence UV-LED UV-400 (365-nm light, 1000 mW cm^{-2}). Visible light irradiation was carried out using a halogen lamp (100 W).

    Materials. Diarylethenes **1a** and **2a** were synthesized as shown in **Scheme S1**. Compound **3** was prepared according to the procedure described in the literature.[S1]
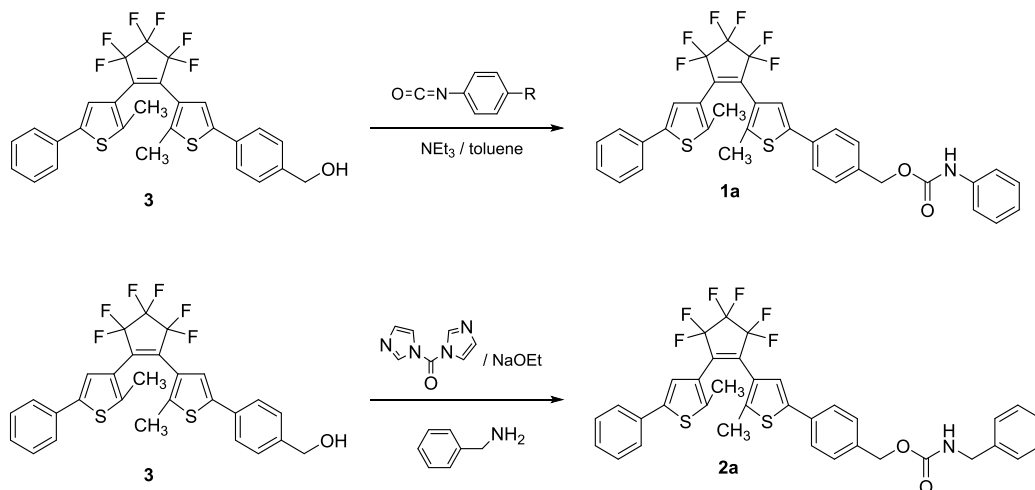
Scheme S1. Synthesis of diarylethenes **1a** and **2a.**

1-(2-Methyl-5-(4-(phenylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)-
*perfluorocyclopentene (**1a**)*

Compound **3** (100 mg, 0.18 mmol) in toluene (3 mL) was added to the solution containing phenyl isocyanate (43 mg, 0.36 mmol) and triethylamine (37 mg, 0.36 mmol) under argon atmosphere and refluxed for 7 h. The reaction 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 hexane/ethyl acetate (8:2) as the eluent. Yield: 63 mg (52%). ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 1.96 (s, 3H, CH$_3$), 1.97 (s, 3H, CH$_3$), 5.21 (s, 2H, CH$_2$), 6.65 (s, 1H, NH), 7.07 (m, 1H, Aromatic), 7.3-7.6 (m, 15H, Aromatic). HRMS (FAB) m/z = 669.1229 ([M]$^+$). Calcd for C$_{35}$H$_{25}$F$_6$NO$_2$S$_2$ = 669.1231.

1-(2-Methyl-5-(4-(benzylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)-
*perfluorocyclopentene (**2a**)*

1,1'-Carbonyldiimidazole (100 mg, 0.61 mmol) and sodium ethoxide were added into a flask containing dry THF (2 mL) under argon atmosphere and stirred for 1 h. Compound **3** (300 mg, 0.54 mmol) in THF (5 mL) was slowly added to the solution and stirred for 7 h, followed by benzylamine (300 mg, 0.54 mmol) was added and stirred for overnight. The unreacted

carbonyldiimidazole was removed by reprecipitation into *n*-hexane solution. The residue was purified by recrystallization from acetone/*n*-hexane solution. Yield: 240 mg (65%). ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 1.95 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$), 4.40 (d, J = 6.2 Hz, 2H, CH$_2$), 5.06 (t, J = 6.2 Hz, 1H, NH), 5.14 (s, 2H, CH$_2$), 7.3-7.7 (m, 16H, Aromatic). HRMS (FAB) m/z = 683.1387 ([M]$^+$). Calcd for C$_{36}$H$_{27}$F$_6$NO$_2$S$_2$ = 683.1387.

Calculation of the lattice energy of crystals. The lattice energy of crystals **1a** and **2a** was calculated using Gaussian 09 according to

$$-E_{\text{latt}} = E_{cryst}/Z - E_{\text{mol}}$$

with E_{cryst} as the energy of the crystal, Z as the number of molecules in the unit cell, and E_{mol} as the energy of the single molecule. The energies of the crystal and the single molecule were calculated as the single point energy using xyz coordinates in the CIF at the DFT/B3LYP/6-31G* level of theory. The lattice energy of crystal **1a** and **2a** was calculated to be 10.95 kJ mol^{-1} for **1a** and 2.35 kJ mol^{-1} for **2a**, respectively.

	1a ($Z = 8$)	**2a** ($Z = 4$)
E_{cryst} (kJ mol^{-1})	-61941401.38	-31383598.09
E_{mol} (kJ mol^{-1})	-7742664.219	-7845897.172
E_{latt} (kJ mol^{-1})	10.95271197	2.349822275

Reference

S1.   S. Kobatake and H. Kuratani, *Chem. Lett.*, 2006, **35**, 628-629.

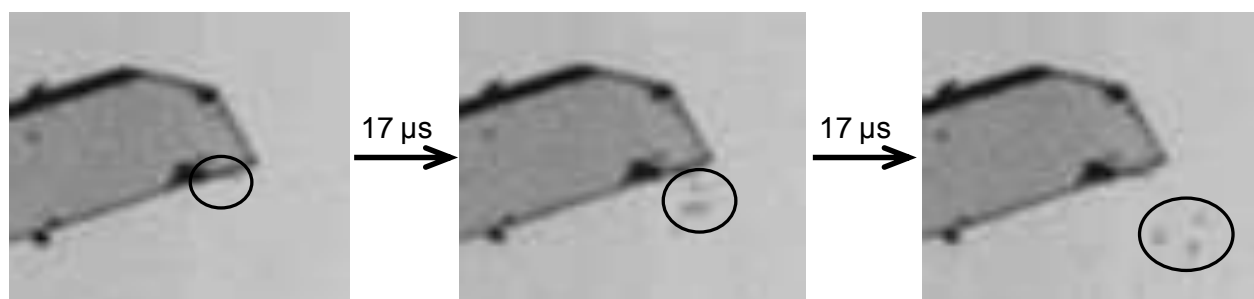**Fig. S1**   Optical photographs taken by high-speed camera.

Table S1. X-ray crystallographic data for **1a** and **2a**.

	1a	2a
Formula	$C_{35}H_{25}F_6NO_2S_2$	$C_{36}H_{27}F_6NO_2S_2$
Formula weight	669.68	683.73
Temperature	150(2) K	123(2) K
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbca$	$P2_1/c$
Unit cell dimensions	$a = 9.246(3)$ Å	$a = 32.197(19)$ Å
	$b = 10.857(3)$ Å	$b = 9.269(5)$ Å
	$c = 60.062(16)$ Å	$c = 10.859(6)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 98.61(5)°$
	$\gamma = 90°$	$\gamma = 90°$
Volume	6029(3) Å^3	3204(3) Å^3
Z	8	4
Density	1.476 g cm^{-3}	1.417 g cm^{-3}
Goodness-of-fit on F^2	1.014	1.087
$R1(I > 2\sigma(I))$	0.0942	0.0632
$wR2$(all data)	0.2616	0.1901
CCDC	1479659	1479658