The Effect of Mechano-stimuli on the Amorphous-to-Crystalline Transition of Mechanochromic Luminescence Materials

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Contents

Experimental Section

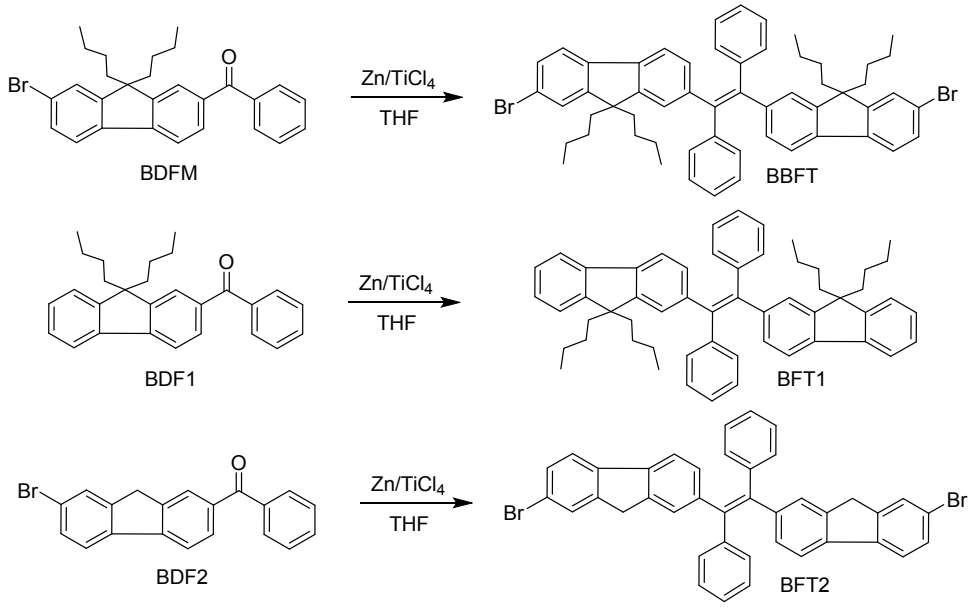
Materials and Instrumentations

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. All reagents were purchased from Aldrich and Acros (>98%) and used as without further purification. In this paper, McMurry coupling was adopted to make the compounds 1,2-bis (7-bromo-9,9-dibutyl-fluorenyl)-1,2-diphenylethene (BBFT), 1,2-bis (9,9-dibutyl-fluorenyl)-1,2-diphenylethene (BFT1), and 1,2-bis (2-fluorenyl-7-bromo)-1,2-diphenylethene (BFT2).

^{1}H and ^{13}C NMR spectroscopy were measured on a Bruker Advance 400 spectrometer in $CDCl_3$ and CD_2Cl_2 with tetramethylsilane (TMS; δ = 0 ppm) as internal reference. Coupling constants (J) are given in hertz (Hz). High resolution mass spectrometry was carried out with a Q-TOF6510 spectrograph (Agilent). Elemental analyses were performed using a Perkin Elmer 2400II elemental analyzer. The crystal structure analysis was carried out on a Bruker SMART APEX-II equipped with CCD area-detector diffractometer at 296(2) K using graphite-monochromated Mo Ká radiation (λ = 0.71073 Å) with the w scan method. The structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 using SHELX programs. The crystallographic datas of BBFT, BFT1, and BFT2 have been deposited in the Cambridge Crystallographic Data centre. X-ray diffraction (XRD) data was collected using a Bruker-AXS D8 ADVANCE X-ray diffractometer at room temperature (Cu-Kα radiation, 1.5418 Å). Data was collected in the 2θ range of 10-50° with a step size of 0.02. Photoluminescence spectra (PL) and fluorescence quantum yield were collected on an Edinburgh Instruments FS920 spectrofluorimeter equipped with Xe-900 and integrating sphere. UV-Vis spectrum was characterized with Shimadzu UV-Vis-2550. Differential scanning calorimetry and thermogravimetry analysis (DSC/TGA) were performed using SDT Q600 V8.1 Build 99 TA Instruments under nitrogen atmosphere.

Luminogen Preparation

The BBFT, BFT1, BFT2 were synthesized according to the synthetic routes shown in Scheme S1.



Scheme S1. Synthetic routes to the compounds BBFT, BFT1, BFT2.

1,2-bis (7-bromo-9,9-dibutyl-fluorenyl)-1,2-diphenylethene (BBFT). 4.4 g (9.56 mmol) of BDFM and 2.4 g (36 mmol) of Zn powder was added to a 250 ml pre-dried three-necked round-bottom flask with a magnetic stirrer and a water condenser. The flask was evacuated under vacuum and flushed with nitrogen for three times. 150 mL of freshly distillated THF was injected into the flask and the mixture was stirred under an ice-bath for a period of time. 2.10 mL (16.8 mmol) of $TiCl_4$ was injected drop-wise into the flask and the mixture was stirred again for 0.5 h on an ice bath. The mixture was refluxed at 80^{o}C overnight. After cooling and solvent evaporation, 150 ml of deionized water and 50 ml of sodium carbonate solution were added to the reaction mixture. Then 10M HCl was added to the reaction mixture to adjust the pH of the solution to be 7. The mixture was extracted with dichloromethane and the organic layer was obtained. The crude product was condensed and purified over silica gel using 10:1 petroleum benzin/DCM as eluent. ^{1}H NMR and ^{13}C NMR of BBFT: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (TMS, ppm): 7.41-7.35 (m, 8H), 7.10-7.03 (m, 14H), 1.78-1.66 (m, 8H), 1.04-0.93 (m, 8H), 0.71-0.62 (m, 12H), 0.47-0.41 (m, 8H). ^{13}C

NMR ($CDCl_3$, 100 MHz) δ (TMS, ppm): 153.20, 153.17, 149.72, 144.16, 143.94, 143.58, 143.55, 141.16, 140.90, 139.98, 139.89, 138.45, 138.34, 131.54, 131.44, 130.66, 130.40, 129.82, 129.76, 127.59, 126.57, 126.50, 126.24, 126.07, 125.99, 125.93, 120.93, 120.82, 120.79, 119.16, 119.02, 55.08, 40.03, 25.92, 25.74, 22.97, 22.90, 13.95, 13.87. HRMS (ESI): 890.2847 ($[M]^+$), calcd. for $C_{56}H_{58}Br_2$ 890.2885. Anal. Calcd. For $C_{56}H_{58}Br_2$: C, 75.50; H, 6.56. Found: C, 75.18; H, 6.97.

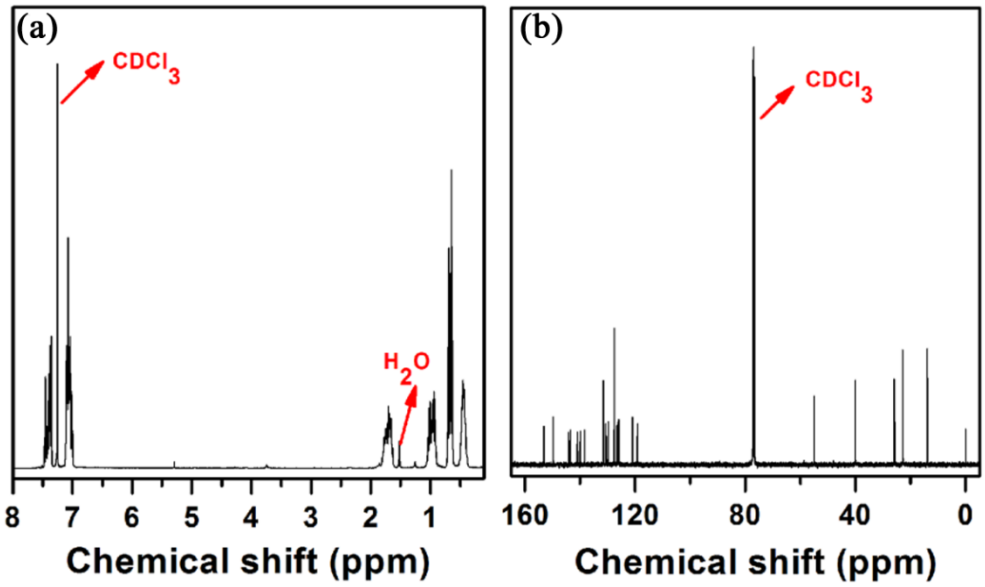


Figure S1. ^1H NMR (a) and ^{13}C NMR (b) spectra of BBFT in $CDCl_3$.

1,2-bis(9,9-dibutyl-fluorenyl)-1,2-diphenylethene1 (BFT1). 3.8g (9.94 mmol) of BDF1 and 2.6 g (39 mmol) of Zn powder was added to a 250 ml pre-dried three-necked round-bottom flask with a magnetic stirrer and a water condenser. The flask was evacuated under vacuum and flushed with nitrogen for three times. 150 mL of freshly distillated THF was injected into the flask and the mixture was stirred under an ice-bath for a period of time. 2.50 mL (19.09 mmol) of $TiCl_4$ was injected drop-wise into the flask and the mixture was stirred again for 0.5 h on an ice bath. The mixture was refluxed at 80^{o}C overnight. After cooling and solvent evaporation, 150 ml of deionized water and 50 ml of sodium carbonate solution were added to the reaction mixture. Then 10M HCl was added to the reaction mixture to adjust the pH of the solution to be 7. The mixture was extracted with dichloromethane and the organic layer was obtained. The crude product was condensed and purified over silica gel using 8:1 petroleum benzin/DCM as eluent. ^1H NMR and ^{13}C NMR of BFT1: ^1H

NMR (CD_2Cl_2, 400 MHz) δ (TMS, ppm): 7.63-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.29-7.26 (m, 6H), 7.10-7.06 (m, 12H), 7.01-6.98 (m, 2H), 1.87-1.78 (m, 4H), 1.72-1.64 (m, 4H), 1.03-0.97 (m, 8H), 0.69-0.64 (m, 12H), 0.45-0.37 (m, 8H). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ (TMS, ppm): 150.95, 150.03, 144.20, 143.19, 141.24, 140.92, 139.34, 131.40, 130.05, 127.48, 126.79, 126.61, 126.44, 126.20, 122.74, 119.40, 118.82, 54.71, 40.04, 26.00, 22.93, 13.71. HRMS (ESI): 733.4710 ($[M]^+$), calcd. for $C_{56}H_{60}$ 732.4695.

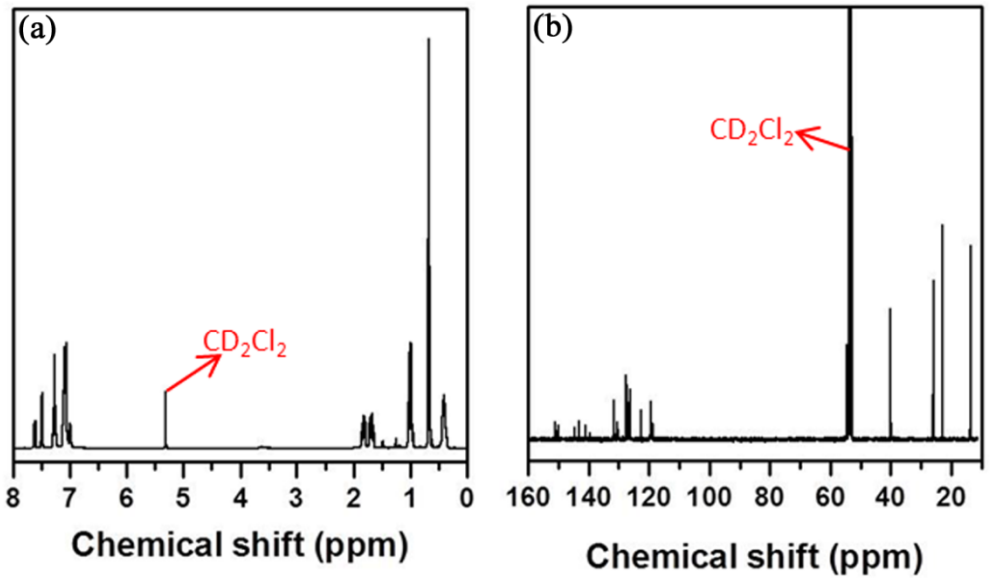


Figure S2. ^1H NMR (a) and ^{13}C NMR (b) spectra of BFT1 in CD_2Cl_2.

1,2-bis (2-fluorenyl-7-bromo)-1,2-diphenylethene (BFT2). 3.5g (10.05 mmol) of BDF2 and 2.6 g (39 mmol) of Zn powder was added to a 250 ml predried three-necked round-bottom flask with a magnetic stirrer and a water condenser. The flask was evacuated under vacuum and flushed with nitrogen for three times. 150 mL of freshly distillated THF was injected into the flask and the mixture was stirred under an ice-bath for a period of time. 2.60 mL (19.85 mmol) of $TiCl_4$ was injected drop-wise into the flask and the mixture was stirred again for 0.5 h on an ice bath. The mixture was refluxed at 80°C overnight. After cooling and solvent evaporation, 150 ml of deionized water and 50 ml of sodium carbonate solution were added to the reaction mixture. Then 10M HCl was added to the reaction mixture to adjust the pH of the solution to be 7. The mixture was extracted with dichloromethane and the organic layer was obtained. The crude product was condensed and purified over silica

gel using 6:1 petroleum benzin/DCM as eluent. ^{1}H NMR and ^{13}C NMR of BFT2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (TMS, ppm): 7.63-7.62 (m, 2H), 7.60-7.44 (m, 6H), 7.24-7.21 (m, 2H), 7.15-7.07 (m, 12H), 3.71-3.70 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (TMS, ppm): 145.54, 145.52, 143.09, 143.87, 143.04, 143.01, 142.33, 141.20, 140.57, 140.51, 139.00, 138.98, 131.42, 130.53, 130.51, 129.84, 128.18, 127.98, 127.90, 127.80, 127.72, 126.51, 121,03, 120.27, 119.20, 119.11, 36.62, 29.70. HRMS (ESI): 666.0363 ($[M]^+$), calcd. for $C_{40}H_{26}Br_2$ 666.0381.

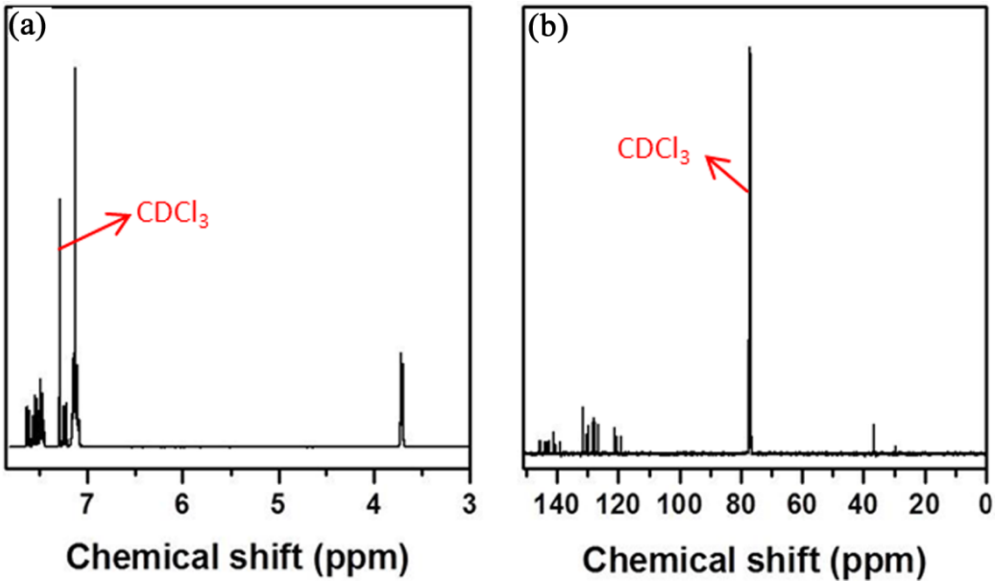


Figure S3. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of BFT2 in $CDCl_3$.

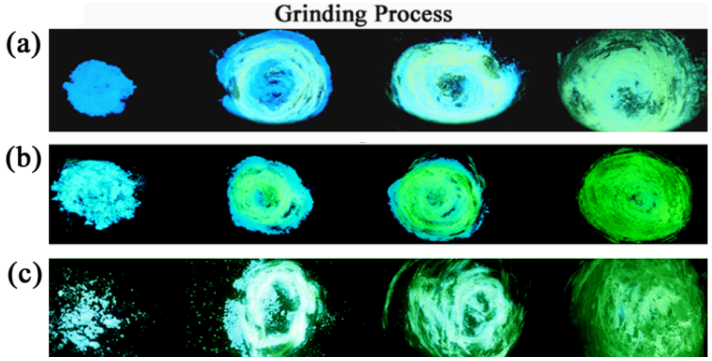


Figure S4. Fluorescence images of BBFT (a), BFT1 (b), and BFT2 (c) in the grinding process.

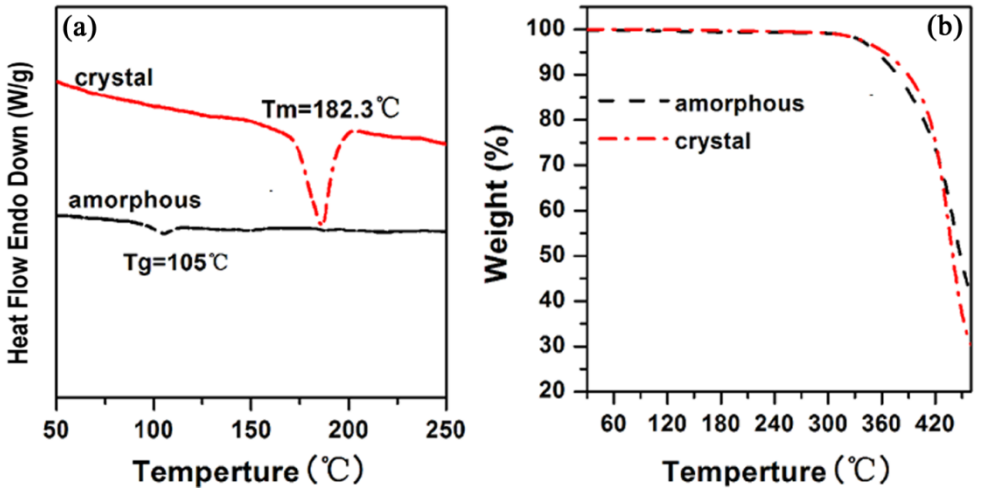


Figure S5. DSC and TGA thermograms of BBFT in the crystalline and amorphous state.

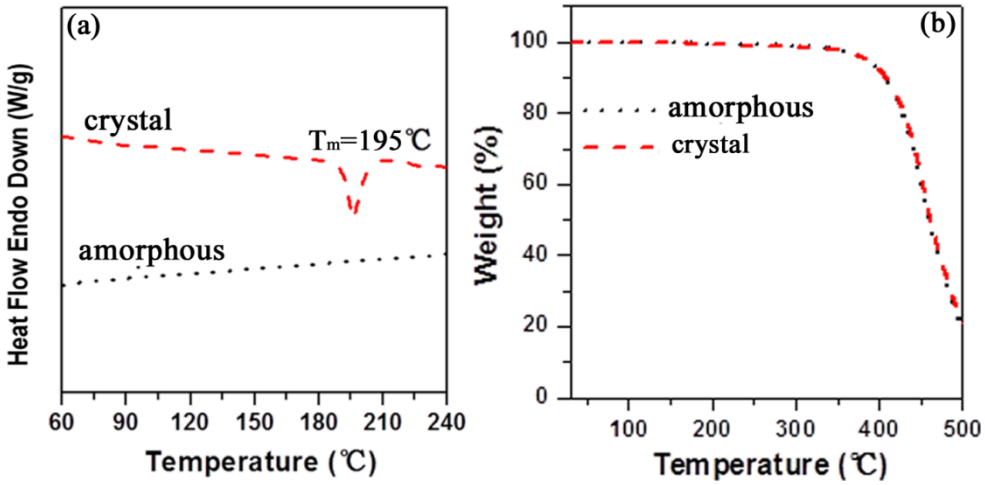


Figure S6. DSC and TGA thermograms of BFT1 in the crystalline and amorphous state.

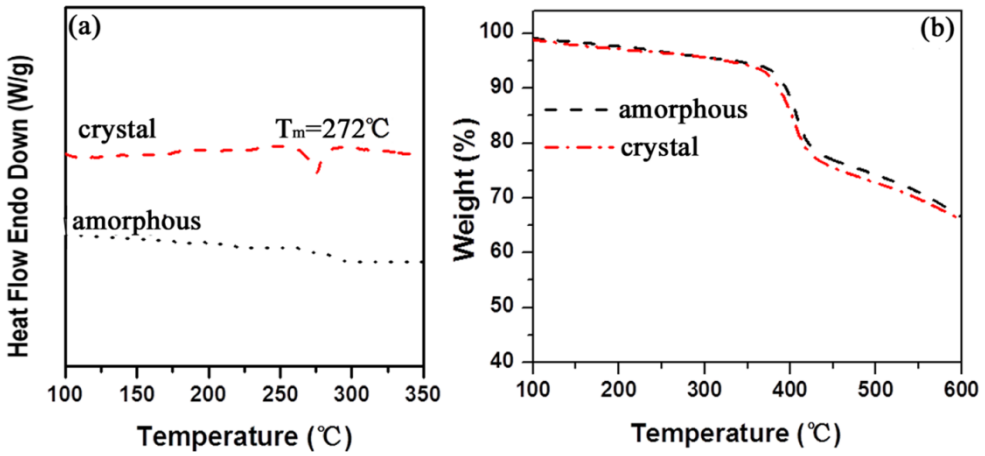


Figure S7. DSC and TGA thermograms of BFT2 in the crystalline and amorphous state.

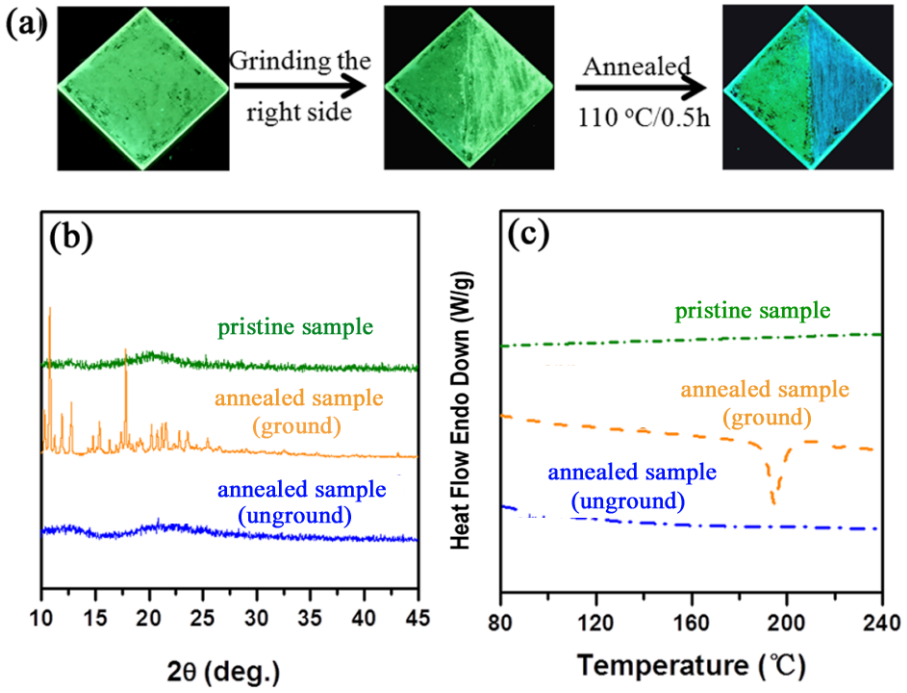


Figure S8. Comparison of the grinding effect on the thermal annealing crystallization by grinding a half side of a pristine BFT1 film and then annealing the whole piece of film (a) and XRD patterns (b) and DSC thermograms of BFT1 (c) under different conditions. Photos were taken under UV irradiation at 365 nm.

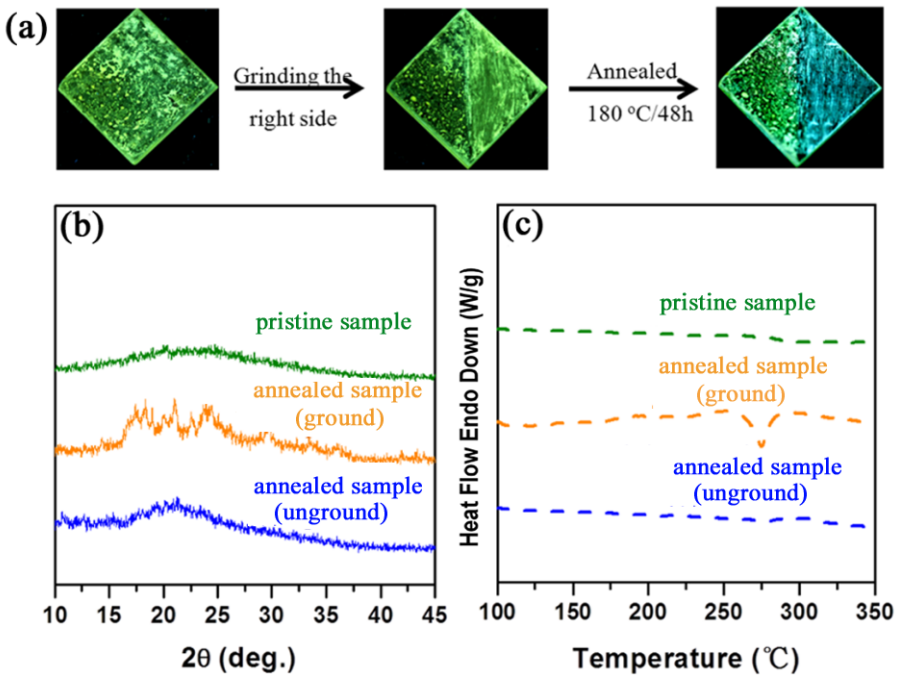


Figure S9. Comparison of the grinding effect on the thermal annealing crystallization by grinding a half side of a pristine BFT2 film and then annealing the whole piece of film (a) and XRD patterns (b) and DSC thermograms of BFT2 (c) under different conditions. Photos were taken under UV irradiation at 365 nm.

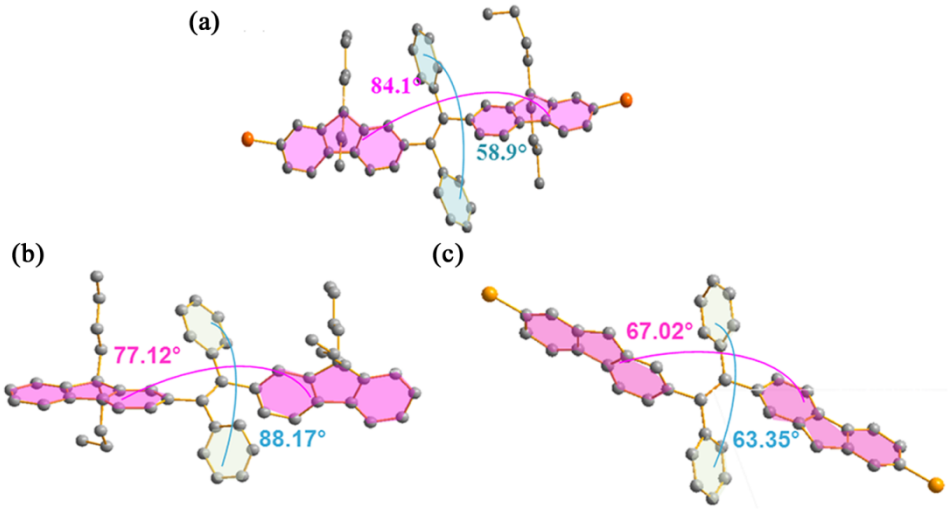


Figure S10. The crystal structures and dihedral angles between the aryl substituents of BBFT (a), BFT1 (b), BFT2 (c).

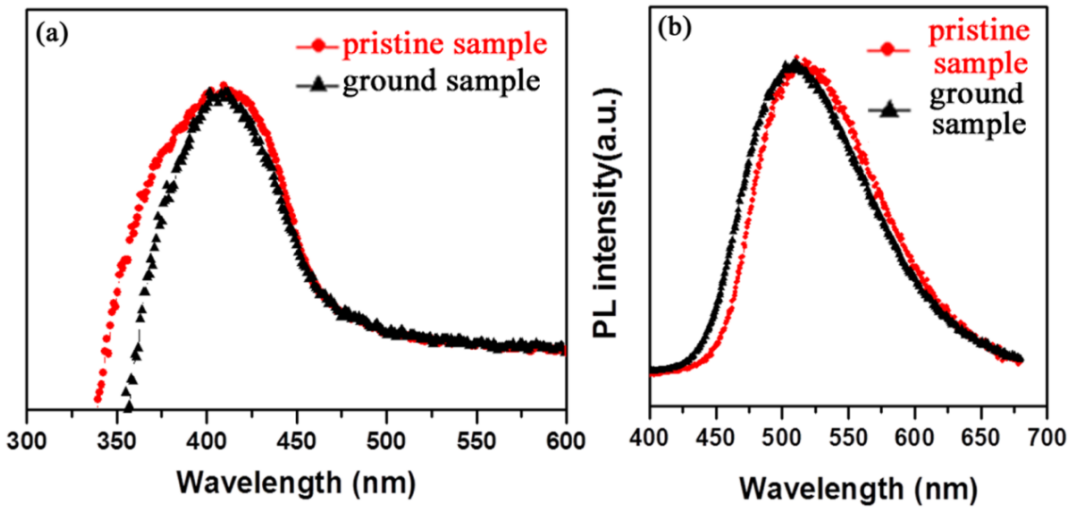


Figure S11. Normalized absorption (a) and emission (b) spectra of BFT1 solids under different conditions.

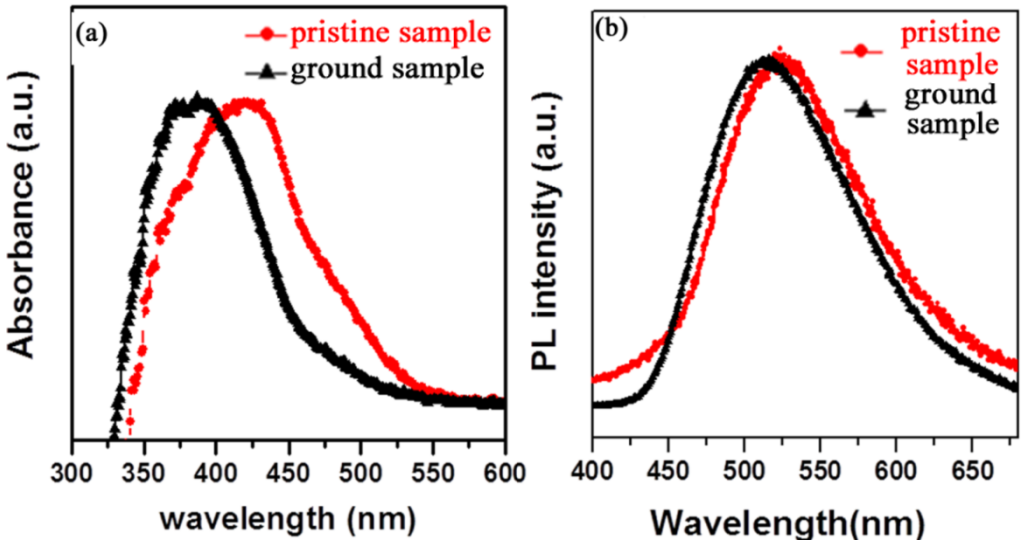


Figure S12. Normalized absorption (a) and emission (b) spectra of BFT2 solids under different conditions.

Table S1. Crystal data and structure refinement for BBFT.

Compound	BBFT
Chemical formula	C56H58Br2
Formula Mass	890.84
Crystal system	Triclinic
Space group	Pī
a/(Å)	8.6456(16)
b/(Å)	12.310(2)
c/(Å)	22.758(4)
α/°	98.677(2)
β/°	92.478(2)
γ/°	104.114(2)
Unit cell volume/(Å^3)	2314.0(7)
T/(K)	296(2)
Z	2
F(000)	928
Absorption coefficient, μ/mm^{-1}	1.787
Reflections measured/independent	22276/7919
R_{int}	0.0456
Final values (all data)	R_1 = 0.0781 wR_2 = 0.1845 R_1 = 0.1170 wR_2 = 0.2075
Goodness of fit on F^2	1.064
CCDC number	909142

Table S2. Crystal data and structure refinement for BFT1.

Compound	BFT1
Chemical formula	C56H60
Formula Mass	733.04
Crystal system	Triclinic
Space group	Pī
a/(Å)	11.1014(9)
b/(Å)	11.6074(9)
c/(Å)	17.9752(14)
α/°	101.9160(10)
β/°	105.0510(10)
γ/°	92.1080(10)
Unit cell volume/(Å^3)	2178.6(3)
T/(K)	296(2)
Z	2
F(000)	792
Absorption coefficient, μ/mm^{-1}	0.063
Reflections measured/independent	25685/9872
R_{int}	0.0196
Final values (all data)	$R_1 = 0.0500$ $wR_2 = 0.1136$ $R_1 = 0.0420$ $wR_2 = 0.1075$
Goodness of fit on F^2	1.041
CCDC number	974227

Table S3. Crystal data and structure refinement for BFT2.

Compound	BFT2
Chemical formula	C40H26Br2
Formula Mass	666.41
Crystal system	Monoclinic
Space group	C2
a/(Å)	25.721(5)
b/(Å)	5.527(5)
c/(Å)	11.027(5)
α/°	90.000(5)
β/°	110.517(5)
γ/°	90.000(5)
Unit cell volume/(Å^3)	1468.2(15)

T/(K)	293(2)
Z	2
F(000)	672
Absorption coefficient, μ/mm^{-1}	2.789
R_{int}	0.000
Final values (all data)	$R_1 = 0.0665$ $wR_2 = 0.1589$ $R_1 = 0.0531$ $wR_2 = 0.1469$
Goodness of fit on F^2	0.829
CCDC number	974229

Table S4. Bond lengths [A] for BBFT molecule.

Br(1)-C(49)	1.910(7)	C(13)-C(45)	1.382(8)	C(32)-C(44)	1.537(8)
C(1)-C(56)	1.366(11)	C(13)-C(34)	1.389(8)	C(33)-C(56)	1.393(10)
C(1)-C(55)	1.368(12)	C(13)-H(13)	0.93	C(33)-H(33)	0.93
C(1)-H(1)	0.93	C(14)-C(49)	1.355(12)	C(34)-H(34)	0.93
C(2)-C(53)	1.371(10)	C(14)-C(20)	1.380(10)	C(35)-C(37)	1.519(11)
C(2)-C(52)	1.391(9)	C(14)-H(14)	0.93	C(35)-H(35A)	0.96
C(2)-C(51)	1.504(9)	C(15)-C(19)	1.405(8)	C(35)-H(35B)	0.96
Br(2)-C(27)	1.895(5)	C(15)-C(51)	1.492(8)	C(35)-H(35C)	0.96
C(3)-C(16)	1.388(8)	C(16)-C(39)	1.390(8)	C(36)-H(36A)	0.96
C(3)-C(21)	1.388(8)	C(16)-C(45)	1.466(8)	C(36)-H(36B)	0.96
C(3)-H(3)	0.93	C(17)-C(21)	1.392(9)	C(36)-H(36C)	0.96
C(4)-C(30)	1.385(9)	C(17)-C(26)	1.396(8)	C(37)-C(41)	1.563(10)
C(4)-C(20)	1.398(9)	C(18)-C(40)	1.480(11)	C(37)-H(37A)	0.97
C(4)-C(23)	1.464(8)	C(18)-C(44)	1.514(9)	C(37)-H(37B)	0.97
C(5)-C(49)	1.377(11)	C(18)-H(18A)	0.97	C(38)-H(38)	0.93
C(5)-C(30)	1.379(9)	C(18)-H(18B)	0.97	C(39)-C(44)	1.531(8)
C(5)-H(5)	0.93	C(19)-C(22)	1.372(8)	C(40)-C(47)	1.557(11)
C(6)-C(51)	1.332(9)	C(19)-H(19)	0.93	C(40)-H(40A)	0.97
C(6)-C(25)	1.484(9)	C(20)-H(20)	0.93	C(40)-H(40B)	0.97
C(6)-C(17)	1.509(8)	C(21)-H(21)	0.93	C(41)-H(41A)	0.97
C(7)-C(36)	1.453(13)	C(22)-C(23)	1.399(8)	C(41)-H(41B)	0.97
C(7)-C(31)	1.551(11)	C(22)-C(46)	1.524(8)	C(42)-C(47)	1.539(10)
C(7)-H(7A)	0.97	C(23)-C(24)	1.375(8)	C(42)-H(42A)	0.96
C(7)-H(7B)	0.97	C(24)-H(24)	0.93	C(42)-H(42B)	0.96
C(8)-C(29)	1.505(9)	C(25)-C(33)	1.384(9)	C(42)-H(42C)	0.96
C(8)-C(50)	1.522(10)	C(26)-C(39)	1.379(8)	C(43)-C(50)	1.495(11)
C(8)-H(8A)	0.97	C(26)-H(26)	0.93	C(43)-H(43A)	0.96
C(8)-H(8B)	0.97	C(27)-C(34)	1.378(9)	C(43)-H(43B)	0.96
C(9)-C(31)	1.489(10)	C(27)-C(38)	1.383(8)	C(43)-H(43C)	0.96
C(9)-C(46)	1.532(8)	C(28)-C(41)	1.497(11)	C(47)-H(47A)	0.97

C(9)-H(9A)	0.97	C(28)-C(44)	1.550(10)	C(47)-H(47B)	0.97
C(9)-H(9B)	0.97	C(28)-H(28A)	0.97	C(48)-C(52)	1.382(11)
C(10)-C(48)	1.359(12)	C(28)-H(28B)	0.97	C(48)-H(48)	0.93
C(10)-C(54)	1.378(12)	C(29)-C(46)	1.545(9)	C(50)-H(50A)	0.97
C(10)-H(10)	0.93	C(29)-H(29A)	0.97	C(50)-H(50B)	0.97
C(11)-C(24)	1.370(9)	C(29)-H(29B)	0.97	C(52)-H(52)	0.93
C(11)-C(15)	1.391(9)	C(30)-C(46)	1.533(8)	C(53)-C(54)	1.397(10)
C(11)-H(11)	0.93	C(31)-H(31A)	0.97	C(53)-H(53)	0.93
C(12)-C(25)	1.383(9)	C(31)-H(31B)	0.97	C(54)-H(54)	0.93
C(12)-C(55)	1.388(10)	C(32)-C(38)	1.377(8)	C(55)-H(55)	0.93
C(12)-H(12)	0.93	C(32)-C(45)	1.402(8)	C(56)-H(56)	0.93

Table S5. Bond angles [deg] for BBFT molecule.

C(56)-C(1)-C(55)	119.2(7)	C(17)-C(21)-H(21)	118.9	C(18)-C(40)-H(40A)	110.1
C(56)-C(1)-H(1)	120.4	C(19)-C(22)-C(23)	120.2(5)	C(47)-C(40)-H(40A)	110.1
C(55)-C(1)-H(1)	120.4	C(19)-C(22)-C(46)	129.1(5)	C(18)-C(40)-H(40B)	110.1
C(53)-C(2)-C(52)	118.4(6)	C(23)-C(22)-C(46)	110.7(5)	C(47)-C(40)-H(40B)	110.1
C(53)-C(2)-C(51)	121.2(6)	C(24)-C(23)-C(22)	120.8(5)	H(40A)-C(40)-H(40B)	108.4
C(52)-C(2)-C(51)	120.4(6)	C(24)-C(23)-C(4)	130.6(5)	C(28)-C(41)-C(37)	115.4(7)
C(16)-C(3)-C(21)	118.2(6)	C(22)-C(23)-C(4)	108.6(5)	C(28)-C(41)-H(41A)	108.4
C(16)-C(3)-H(3)	120.9	C(11)-C(24)-C(23)	118.8(6)	C(37)-C(41)-H(41A)	108.4
C(21)-C(3)-H(3)	120.9	C(11)-C(24)-H(24)	120.6	C(28)-C(41)-H(41B)	108.4
C(30)-C(4)-C(20)	120.5(6)	C(23)-C(24)-H(24)	120.6	C(37)-C(41)-H(41B)	108.4
C(30)-C(4)-C(23)	108.7(5)	C(12)-C(25)-C(33)	117.5(6)	H(41A)-C(41)-H(41B)	107.5
C(20)-C(4)-C(23)	130.7(6)	C(12)-C(25)-C(6)	122.3(6)	C(47)-C(42)-H(42A)	109.5
C(49)-C(5)-C(30)	118.3(7)	C(33)-C(25)-C(6)	120.1(6)	C(47)-C(42)-H(42B)	109.5
C(49)-C(5)-H(5)	120.8	C(39)-C(26)-C(17)	119.9(6)	H(42A)-C(42)-H(42B)	109.5
C(30)-C(5)-H(5)	120.8	C(39)-C(26)-H(26)	120.1	C(47)-C(42)-H(42C)	109.5
C(51)-C(6)-C(25)	126.2(5)	C(17)-C(26)-H(26)	120.1	H(42A)-C(42)-H(42C)	109.5
C(51)-C(6)-C(17)	120.3(6)	C(34)-C(27)-C(38)	122.4(5)	H(42B)-C(42)-H(42C)	109.5
C(25)-C(6)-C(17)	113.5(5)	C(34)-C(27)-Br(2)	118.6(4)	C(50)-C(43)-H(43A)	109.5
C(36)-C(7)-C(31)	112.9(8)	C(38)-C(27)-Br(2)	119.0(4)	C(50)-C(43)-H(43B)	109.5
C(36)-C(7)-H(7A)	109	C(41)-C(28)-C(44)	116.6(5)	H(43A)-C(43)-H(43B)	109.5
C(31)-C(7)-H(7A)	109	C(41)-C(28)-H(28A)	108.1	C(50)-C(43)-H(43C)	109.5
C(36)-C(7)-H(7B)	109	C(44)-C(28)-H(28A)	108.1	H(43A)-C(43)-H(43C)	109.5
C(31)-C(7)-H(7B)	109	C(41)-C(28)-H(28B)	108.1	H(43B)-C(43)-	109.5

				H(43C)	
H(7A)-C(7)-H(7B)	107.8	C(44)-C(28)-H(28B)	108.1	C(18)-C(44)-C(39)	112.2(5)
C(29)-C(8)-C(50)	110.8(6)	H(28A)-C(28)-H(28B)	107.3	C(18)-C(44)-C(32)	111.9(5)
C(29)-C(8)-H(8A)	109.5	C(8)-C(29)-C(46)	116.2(5)	C(39)-C(44)-C(32)	100.0(5)
C(50)-C(8)-H(8A)	109.5	C(8)-C(29)-H(29A)	108.2	C(18)-C(44)-C(28)	107.8(6)
C(29)-C(8)-H(8B)	109.5	C(46)-C(29)-H(29A)	108.2	C(39)-C(44)-C(28)	111.7(5)
C(50)-C(8)-H(8B)	109.5	C(8)-C(29)-H(29B)	108.2	C(32)-C(44)-C(28)	113.1(5)
H(8A)-C(8)-H(8B)	108.1	C(46)-C(29)-H(29B)	108.2	C(13)-C(45)-C(32)	120.0(5)
C(31)-C(9)-C(46)	116.9(5)	H(29A)-C(29)-H(29B)	107.4	C(13)-C(45)-C(16)	132.0(6)
C(31)-C(9)-H(9A)	108.1	C(5)-C(30)-C(4)	119.9(6)	C(32)-C(45)-C(16)	107.9(5)
C(46)-C(9)-H(9A)	108.1	C(5)-C(30)-C(46)	128.9(6)	C(22)-C(46)-C(9)	114.0(5)
C(31)-C(9)-H(9B)	108.1	C(4)-C(30)-C(46)	111.1(5)	C(22)-C(46)-C(30)	100.8(5)
C(46)-C(9)-H(9B)	108.1	C(9)-C(31)-C(7)	111.8(6)	C(9)-C(46)-C(30)	111.2(5)
H(9A)-C(9)-H(9B)	107.3	C(9)-C(31)-H(31A)	109.3	C(22)-C(46)-C(29)	110.4(5)
C(48)-C(10)-C(54)	120.5(7)	C(7)-C(31)-H(31A)	109.3	C(9)-C(46)-C(29)	107.5(5)
C(48)-C(10)-H(10)	119.7	C(9)-C(31)-H(31B)	109.3	C(30)-C(46)-C(29)	113.0(5)
C(54)-C(10)-H(10)	119.7	C(7)-C(31)-H(31B)	109.3	C(42)-C(47)-C(40)	110.0(8)
C(24)-C(11)-C(15)	122.0(6)	H(31A)-C(31)-H(31B)	107.9	C(42)-C(47)-H(47A)	109.7
C(24)-C(11)-H(11)	119	C(38)-C(32)-C(45)	120.7(5)	C(40)-C(47)-H(47A)	109.7
C(15)-C(11)-H(11)	119	C(38)-C(32)-C(44)	127.9(5)	C(42)-C(47)-H(47B)	109.7
C(25)-C(12)-C(55)	120.7(7)	C(45)-C(32)-C(44)	111.4(5)	C(40)-C(47)-H(47B)	109.7
C(25)-C(12)-H(12)	119.7	C(25)-C(33)-C(56)	121.5(7)	H(47A)-C(47)-H(47B)	108.2
C(55)-C(12)-H(12)	119.7	C(25)-C(33)-H(33)	119.2	C(10)-C(48)-C(52)	120.3(8)
C(45)-C(13)-C(34)	119.6(6)	C(56)-C(33)-H(33)	119.2	C(10)-C(48)-H(48)	119.9
C(45)-C(13)-H(13)	120.2	C(27)-C(34)-C(13)	119.2(5)	C(52)-C(48)-H(48)	119.9
C(34)-C(13)-H(13)	120.2	C(27)-C(34)-H(34)	120.4	C(14)-C(49)-C(5)	122.8(7)
C(49)-C(14)-	119.5(7)	C(13)-C(34)-H(34)	120.4	C(14)-C(49)-Br(1)	117.6(6)

C(20)					
C(49)-C(14)-H(14)	120.3	C(37)-C(35)-H(35A)	109.5	C(5)-C(49)-Br(1)	119.5(7)
C(20)-C(14)-H(14)	120.3	C(37)-C(35)-H(35B)	109.5	C(43)-C(50)-C(8)	113.5(7)
C(11)-C(15)-C(19)	118.7(5)	H(35A)-C(35)-H(35B)	109.5	C(43)-C(50)-H(50A)	108.9
C(11)-C(15)-C(51)	118.2(5)	C(37)-C(35)-H(35C)	109.5	C(8)-C(50)-H(50A)	108.9
C(19)-C(15)-C(51)	123.0(5)	H(35A)-C(35)-H(35C)	109.5	C(43)-C(50)-H(50B)	108.9
C(3)-C(16)-C(39)	120.4(5)	H(35B)-C(35)-H(35C)	109.5	C(8)-C(50)-H(50B)	108.9
C(3)-C(16)-C(45)	130.6(6)	C(7)-C(36)-H(36A)	109.5	H(50A)-C(50)-H(50B)	107.7
C(39)-C(16)-C(45)	109.0(5)	C(7)-C(36)-H(36B)	109.5	C(6)-C(51)-C(15)	124.5(6)
C(21)-C(17)-C(26)	118.4(5)	H(36A)-C(36)-H(36B)	109.5	C(6)-C(51)-C(2)	120.5(5)
C(21)-C(17)-C(6)	122.0(5)	C(7)-C(36)-H(36C)	109.5	C(15)-C(51)-C(2)	115.0(5)
C(26)-C(17)-C(6)	119.6(5)	H(36A)-C(36)-H(36C)	109.5	C(48)-C(52)-C(2)	120.6(8)
C(40)-C(18)-C(44)	114.5(6)	H(36B)-C(36)-H(36C)	109.5	C(48)-C(52)-H(52)	119.7
C(40)-C(18)-H(18A)	108.6	C(35)-C(37)-C(41)	111.0(7)	C(2)-C(52)-H(52)	119.7
C(44)-C(18)-H(18A)	108.6	C(35)-C(37)-H(37A)	109.4	C(2)-C(53)-C(54)	121.2(7)
C(40)-C(18)-H(18B)	108.6	C(41)-C(37)-H(37A)	109.4	C(2)-C(53)-H(53)	119.4
C(44)-C(18)-H(18B)	108.6	C(35)-C(37)-H(37B)	109.4	C(54)-C(53)-H(53)	119.4
H(18A)-C(18)-H(18B)	107.6	C(41)-C(37)-H(37B)	109.4	C(10)-C(54)-C(53)	119.0(8)
C(22)-C(19)-C(15)	119.6(5)	H(37A)-C(37)-H(37B)	108	C(10)-C(54)-H(54)	120.5
C(22)-C(19)-H(19)	120.2	C(32)-C(38)-C(27)	118.1(6)	C(53)-C(54)-H(54)	120.5
C(15)-C(19)-H(19)	120.2	C(32)-C(38)-H(38)	121	C(1)-C(55)-C(12)	121.1(7)
C(14)-C(20)-C(4)	118.9(7)	C(27)-C(38)-H(38)	121	C(1)-C(55)-H(55)	119.5
C(14)-C(20)-H(20)	120.5	C(26)-C(39)-C(16)	120.8(6)	C(12)-C(55)-H(55)	119.5
C(4)-C(20)-H(20)	120.5	C(26)-C(39)-C(44)	127.7(6)	C(1)-C(56)-C(33)	120.0(8)

C(3)-C(21)-C(17)	122.2(6)	C(16)-C(39)-C(44)	111.5(5)	C(1)-C(56)-H(56)	120
C(3)-C(21)-H(21)	118.9	C(18)-C(40)-C(47)	108.0(7)	C(33)-C(56)-H(56)	120

Table S6. Bond lengths [A] for the optimized BBFT molecule.

Br(1)-C(49)	1.95	C(13)-C(45)	1.398	C(32)-C(44)	1.533
C(1)-C(56)	1.401	C(13)-C(34)	1.401	C(33)-C(56)	1.398
C(1)-C(55)	1.401	C(13)-H(13)	1.085	C(33)-H(33)	1.085
C(1)-H(1)	1.085	C(14)-C(49)	1.395	C(34)-H(34)	1.083
C(2)-C(53)	1.41	C(14)-C(20)	1.401	C(35)-C(37)	1.539
C(2)-C(52)	1.409	C(14)-H(14)	1.083	C(35)-H(35A)	1.096
C(2)-C(51)	1.498	C(15)-C(19)	1.414	C(35)-H(35B)	1.096
Br(2)-C(27)	1.95	C(15)-C(51)	1.496	C(35)-H(35C)	1.097
C(3)-C(16)	1.398	C(16)-C(39)	1.415	C(36)-H(36A)	1.097
C(3)-C(21)	1.398	C(16)-C(45)	1.469	C(36)-H(36B)	1.096
C(3)-H(3)	1.086	C(17)-C(21)	1.411	C(36)-H(36C)	1.097
C(4)-C(30)	1.416	C(17)-C(26)	1.414	C(37)-C(41)	1.544
C(4)-C(20)	1.398	C(18)-C(40)	1.538	C(37)-H(37A)	1.099
C(4)-C(23)	1.468	C(18)-C(44)	1.565	C(37)-H(37B)	1.1
C(5)-C(49)	1.397	C(18)-H(18A)	1.1	C(38)-H(38)	1.084
C(5)-C(30)	1.392	C(18)-H(18B)	1.1	C(39)-C(44)	1.534
C(5)-H(5)	1.084	C(19)-C(22)	1.39	C(40)-C(47)	1.541
C(6)-C(51)	1.371	C(19)-H(19)	1.085	C(40)-H(40A)	1.099
C(6)-C(25)	1.497	C(20)-H(20)	1.085	C(40)-H(40B)	1.098
C(6)-C(17)	1.496	C(21)-H(21)	1.084	C(41)-H(41A)	1.098
C(7)-C(36)	1.537	C(22)-C(23)	1.415	C(41)-H(41B)	1.099
C(7)-C(31)	1.541	C(22)-C(46)	1.535	C(42)-C(47)	1.537
C(7)-H(7A)	1.1	C(23)-C(24)	1.398	C(42)-H(42A)	1.097
C(7)-H(7B)	1.1	C(24)-H(24)	1.086	C(42)-H(42B)	1.096
C(8)-C(29)	1.538	C(25)-C(33)	1.41	C(42)-H(42C)	1.098
C(8)-C(50)	1.541	C(26)-C(39)	1.389	C(43)-C(50)	1.537
C(8)-H(8A)	1.099	C(26)-H(26)	1.086	C(43)-H(43A)	1.097
C(8)-H(8B)	1.098	C(27)-C(34)	1.395	C(43)-H(43B)	1.096
C(9)-C(31)	1.538	C(27)-C(38)	1.397	C(43)-H(43C)	1.097
C(9)-C(46)	1.564	C(28)-C(41)	1.539	C(47)-H(47A)	1.1
C(9)-H(9A)	1.1	C(28)-C(44)	1.563	C(47)-H(47B)	1.1
C(9)-H(9B)	1.1	C(28)-H(28A)	1.101	C(48)-C(52)	1.397
C(10)-C(48)	1.4	C(28)-H(28B)	1.098	C(48)-H(48)	1.086
C(10)-C(54)	1.4	C(29)-C(46)	1.563	C(50)-H(50A)	1.1
C(10)-H(10)	1.085	C(29)-H(29A)	1.1	C(50)-H(50B)	1.1
C(11)-C(24)	1.397	C(29)-H(29B)	1.1	C(52)-H(52)	1.085
C(11)-C(15)	1.413	C(30)-C(46)	1.533	C(53)-C(54)	1.398
C(11)-H(11)	1.085	C(31)-H(31A)	1.099	C(53)-H(53)	1.085
C(12)-C(25)	1.409	C(31)-H(31B)	1.099	C(54)-H(54)	1.086

C(12)-C(55)	1.398	C(32)-C(38)	1.392	C(55)-H(55)	1.086
C(12)-H(12)	1.084	C(32)-C(45)	1.416	C(56)-H(56)	1.086

Table S7. Bond angles [deg] for the optimized BBFT molecule.

C(56)-C(1)-C(55)	119.5	C(17)-C(21)-H(21)	118.9	C(18)-C(40)-H(40A)	110.0
C(56)-C(1)-H(1)	120.3	C(19)-C(22)-C(23)	120.4	C(47)-C(40)-H(40A)	109.2
C(55)-C(1)-H(1)	120.2	C(19)-C(22)-C(46)	128.6	C(18)-C(40)-H(40B)	110.0
C(53)-C(2)-C(52)	118.2	C(23)-C(22)-C(46)	110.9	C(47)-C(40)-H(40B)	109.1
C(53)-C(2)-C(51)	120.6	C(24)-C(23)-C(22)	120.2	H(40A)-C(40)-H(40B)	106.5
C(52)-C(2)-C(51)	121.2	C(24)-C(23)-C(4)	131.2	C(28)-C(41)-C(37)	113.6
C(16)-C(3)-C(21)	119.1	C(22)-C(23)-C(4)	108.6	C(28)-C(41)-H(41A)	109.2
C(16)-C(3)-H(3)	121.0	C(11)-C(24)-C(23)	119.1	C(37)-C(41)-H(41A)	108.8
C(21)-C(3)-H(3)	119.9	C(11)-C(24)-H(24)	119.9	C(28)-C(41)-H(41B)	109.4
C(30)-C(4)-C(20)	120.5	C(23)-C(24)-H(24)	121.0	C(37)-C(41)-H(41B)	109.0
C(30)-C(4)-C(23)	108.4	C(12)-C(25)-C(33)	118.2	H(41A)-C(41)-H(41B)	106.6
C(20)-C(4)-C(23)	131.1	C(12)-C(25)-C(6)	121.2	C(47)-C(42)-H(42A)	111.0
C(49)-C(5)-C(30)	118.1	C(33)-C(25)-C(6)	120.5	C(47)-C(42)-H(42B)	111.4
C(49)-C(5)-H(5)	120.1	C(39)-C(26)-C(17)	120.1	H(42A)-C(42)-H(42B)	107.8
C(30)-C(5)-H(5)	121.8	C(39)-C(26)-H(26)	120.8	C(47)-C(42)-H(42C)	111.0
C(51)-C(6)-C(25)	122.8	C(17)-C(26)-H(26)	119.2	H(42A)-C(42)-H(42C)	107.6
C(51)-C(6)-C(17)	122.6	C(34)-C(27)-C(38)	122.5	H(42B)-C(42)-H(42C)	107.8
C(25)-C(6)-C(17)	114.5	C(34)-C(27)-Br(2)	118.9	C(50)-C(43)-H(43A)	110.9
C(36)-C(7)-C(31)	112.9	C(38)-C(27)-Br(2)	118.6	C(50)-C(43)-H(43B)	111.4
C(36)-C(7)-H(7A)	109.5	C(41)-C(28)-C(44)	115.9	H(43A)-C(43)-H(43B)	107.8

C(31)-C(7)-H(7A)	109.3	C(41)-C(28)-H(28A)	109.2	C(50)-C(43)-H(43C)	111.1
C(36)-C(7)-H(7B)	109.5	C(44)-C(28)-H(28A)	107.9	H(43A)-C(43)-H(43C)	107.6
C(31)-C(7)-H(7B)	109.3	C(41)-C(28)-H(28B)	109.7	H(43B)-C(43)-H(43C)	107.8
H(7A)-C(7)-H(7B)	106.2	C(44)-C(28)-H(28B)	107.4	C(18)-C(44)-C(39)	111.8
C(29)-C(8)-C(50)	112.3	H(28A)-C(28)-H(28B)	106.3	C(18)-C(44)-C(32)	111.7
C(29)-C(8)-H(8A)	109.7	C(8)-C(29)-C(46)	116.3	C(39)-C(44)-C(32)	101.0
C(50)-C(8)-H(8A)	109.1	C(8)-C(29)-H(29A)	109.1	C(18)-C(44)-C(28)	107.9
C(29)-C(8)-H(8B)	109.7	C(46)-C(29)-H(29A)	107.8	C(39)-C(44)-C(28)	112.2
C(50)-C(8)-H(8B)	109.1	C(8)-C(29)-H(29B)	109.2	C(32)-C(44)-C(28)	112.2
H(8A)-C(8)-H(8B)	106.7	C(46)-C(29)-H(29B)	107.8	C(13)-C(45)-C(32)	120.5
C(31)-C(9)-C(46)	116.2	H(29A)-C(29)-H(29B)	106.3	C(13)-C(45)-C(16)	131.1
C(31)-C(9)-H(9A)	109.2	C(5)-C(30)-C(4)	120.4	C(32)-C(45)-C(16)	108.4
C(46)-C(9)-H(9A)	107.7	C(5)-C(30)-C(46)	128.6	C(22)-C(46)-C(9)	111.8
C(31)-C(9)-H(9B)	109.2	C(4)-C(30)-C(46)	111.0	C(22)-C(46)-C(30)	101.0
C(46)-C(9)-H(9B)	107.8	C(9)-C(31)-C(7)	112.5	C(9)-C(46)-C(30)	111.8
H(9A)-C(9)-H(9B)	106.3	C(9)-C(31)-H(31A)	109.6	C(22)-C(46)-C(29)	112.3
C(48)-C(10)-C(54)	119.5	C(7)-C(31)-H(31A)	109.2	C(9)-C(46)-C(29)	108.0
C(48)-C(10)-H(10)	120.2	C(9)-C(31)-H(31B)	109.7	C(30)-C(46)-C(29)	111.9
C(54)-C(10)-H(10)	120.2	C(7)-C(31)-H(31B)	109.1	C(42)-C(47)-C(40)	112.9
C(24)-C(11)-C(15)	121.5	H(31A)-C(31)-H(31B)	106.5	C(42)-C(47)-H(47A)	109.5
C(24)-C(11)-H(11)	119.6	C(38)-C(32)-C(45)	120.4	C(40)-C(47)-H(47A)	109.3
C(15)-C(11)-H(11)	119.0	C(38)-C(32)-C(44)	128.6	C(42)-C(47)-H(47B)	109.5
C(25)-C(12)-C(55)	120.9	C(45)-C(32)-C(44)	111.0	C(40)-C(47)-H(47B)	109.3
C(25)-C(12)-H(12)	119.2	C(25)-C(33)-C(56)	120.9	H(47A)-C(47)-H(47B)	106.2
C(55)-C(12)-H(12)	119.9	C(25)-C(33)-H(33)	119.2	C(10)-C(48)-C(52)	120.3
C(45)-C(13)-C(34)	119.3	C(56)-C(33)-H(33)	119.9	C(10)-C(48)-H(48)	120.1
C(45)-C(13)-H(13)	121.0	C(27)-C(34)-C(13)	119.3	C(52)-C(48)-H(48)	119.7
C(34)-C(13)-H(13)	119.7	C(27)-C(34)-H(34)	120.0	C(14)-C(49)-C(5)	122.5
C(49)-C(14)-C(20)	119.3	C(13)-C(34)-H(34)	120.7	C(14)-C(49)-Br(1)	118.9
C(49)-C(14)-H(14)	120.0	C(37)-C(35)-H(35A)	111.9	C(5)-C(49)-Br(1)	118.7
C(20)-C(14)-H(14)	120.7	C(37)-C(35)-H(35B)	111.0	C(43)-C(50)-C(8)	112.9
C(11)-C(15)-C(19)	118.7	H(35A)-C(35)-H(35B)	107.4	C(43)-C(50)-H(50A)	109.4
C(11)-C(15)-C(51)	120.1	C(37)-C(35)-H(35C)	111.0	C(8)-C(50)-H(50A)	109.3
C(19)-C(15)-C(51)	121.0	H(35A)-C(35)-H(35C)	107.5	C(43)-C(50)-H(50B)	109.5

C(3)-C(16)-C(39)	120.2	H(35B)-C(35)-H(35C)	107.9	C(8)-C(50)-H(50B)	109.1
C(3)-C(16)-C(45)	131.3	C(7)-C(36)-H(36A)	111.0	H(50A)-C(50)-H(50B)	106.4
C(39)-C(16)-C(45)	108.6	C(7)-C(36)-H(36B)	111.4	C(6)-C(51)-C(15)	122.9
C(21)-C(17)-C(26)	118.8	H(36A)-C(36)-H(36B)	107.8	C(6)-C(51)-C(2)	122.4
C(21)-C(17)-C(6)	121.0	C(7)-C(36)-H(36C)	111.1	C(15)-C(51)-C(2)	114.8
C(26)-C(17)-C(6)	120.2	H(36A)-C(36)-H(36C)	107.6	C(48)-C(52)-C(2)	120.9
C(40)-C(18)-C(44)	116.3	H(36B)-C(36)-H(36C)	107.8	C(48)-C(52)-H(52)	119.9
C(40)-C(18)-H(18A)	109.2	C(35)-C(37)-C(41)	114.4	C(2)-C(52)-H(52)	119.2
C(44)-C(18)-H(18A)	107.6	C(35)-C(37)-H(37A)	109.0	C(2)-C(53)-C(54)	120.9
C(40)-C(18)-H(18B)	109.2	C(41)-C(37)-H(37A)	108.3	C(2)-C(53)-H(53)	119.2
C(44)-C(18)-H(18B)	107.9	C(35)-C(37)-H(37B)	109.5	C(54)-C(53)-H(53)	119.9
H(18A)-C(18)-H(18B)	106.3	C(41)-C(37)-H(37B)	109.3	C(10)-C(54)-C(53)	120.2
C(22)-C(19)-C(15)	120.0	H(37A)-C(37)-H(37B)	106.1	C(10)-C(54)-H(54)	120.1
C(22)-C(19)-H(19)	120.9	C(32)-C(38)-C(27)	118.1	C(53)-C(54)-H(54)	119.7
C(15)-C(19)-H(19)	119.1	C(32)-C(38)-H(38)	121.8	C(1)-C(55)-C(12)	120.3
C(14)-C(20)-C(4)	119.3	C(27)-C(38)-H(38)	120.1	C(1)-C(55)-H(55)	120.0
C(14)-C(20)-H(20)	119.7	C(26)-C(39)-C(16)	120.4	C(12)-C(55)-H(55)	119.7
C(4)-C(20)-H(20)	121.0	C(26)-C(39)-C(44)	128.6	C(1)-C(56)-C(33)	120.2
C(3)-C(21)-C(17)	121.4	C(16)-C(39)-C(44)	111.0	C(1)-C(56)-H(56)	120.1
C(3)-C(21)-H(21)	119.7	C(18)-C(40)-C(47)	112.5	C(33)-C(56)-H(56)	119.7