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Supporting Information

Fast photoactuation of the elastic crystals based on 3-(naphthalen-1-yl)-2phenylacrylonitriles triggered by subtle photoisomerization

Cheng Liu, Kaiqi Ye,* Zhonglin Wei, Jiang Peng, Huan Xiao, Jingbo Sun and Ran Lu*

Sate Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin

University, Changchun, China.

E-mail: yekq@jlu.edu.cn; luran@mail.jlu.edu.cn

Video S1. The photo-induced bending backward from the light source of the slice-like crystal of *Z*-**FPhNaF** upon irradiated by 365 nm light ($1.5 \times$ speed).

Video S2. The photo-induced bending backward from the light source of slice-like crystal of Z-**FPhNaF** upon irradiation of 410 nm light (1.5× speed).

Video S3. The photo-induced bending backward from the light source of a thin slice-like crystal of *Z*-**FPhNaF** upon irradiation of 365 nm light.

Video S4. The photo-induced bending backward from the light source of the needle-like crystal of *Z*-**FPhNaOMe** upon irradiation of 365 nm light (1.5× speed).

Video S5. The photo-induced bending backward from the light source of the needle-like crystal of *Z***-FPhNaOMe** upon irradiation of 410 nm light.

Video S6. The photo-induced reversible bending of the slice-like crystal of *Z*-**FPhNaF** upon irradiating with 365 nm light from left and right alternately (25× speed).

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Video S8. The photo-induced bending backward from the light source of the needle-like crystal of *Z*-**FPhNaOMe** upon irradiation of 365 nm light in water (2× speed).

Video S9. The photo-induced bending backward from the light source of the slice-like crystal of *Z*-**HPhNaH** upon irradiation of 410 nm light (2× speed).

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Video S14. The photo-induced bending backward from the light source of the needle-like

crystal of *Z*-**BrPhNaH** upon irradiation of 410 nm light (2× speed).

Video S15. The photo-induced bending backward from the light source of the needle-like crystal of *Z*-**BrPhNaF** upon irradiation of 410 nm light (2× speed).

Video S16. The thermo-induced unbending of the slice-like crystal of *Z***-FPhNaF** at 80 °C.

General Information

¹H NMR and ¹³C NMR spectra were recorded with a Bruker-Avance III 400 MHz and 101 MHz spectrometers using CDCl₃ and DMSO-d₆ as solvents and tetramethylsilane (TMS) as the internal standard. The samples for irradiation time-dependent ¹H NMR measurements were gained via the irradiation of the microcrystals of Z-HPhNaH, Z-HPhNaF, Z-FPhNaH, Z-ClPhNaH, B Z-rPhNaH, Z-FPhNaF, Z-ClPhNaF, Z-BrPhNaF and Z-FPhNaOMe by 365 nm (16.7 mW/cm²) light for different times, followed by dissolving in DMSO-d₆. FT-IR spectra were obtained with a Nicolet-360 FT-IR spectrometer by the incorporation of samples into KBr disks. High-resolution mass analyses was performed on Agilent1290-Bruker micrOTOF QII apparatus. The HPLC experiments were performed using an Agilent 1290 Infinity LC system. Chromatographic separation was achieved on a Zorbax Stable Bond C18 analytical column (2.1×150 mm, 1.8 µm; Aglient Technologies, USA) operated at 30 °C. The UV detector wavelength was set to be 340 nm. The gradient elution mode was applied, and aqueous solution of formic acid (0.1%)-acetonitrile was used as mobile phase. In the initial 0-60 min, the mobile phase contained 30-90% (vol %) of acetonitrile. At 60-80 min, the vol% of acetonitrile was maintained at 90%. The flow rate was 0.25 mL/min. UV-vis absorption spectra were measured by a Shimadzu UV-1601PC spectrophotometer. Fluorescence emission spectra were taken on a Shimadzu RF5301 luminescence spectrometer. The solid-state samples for the absorption and emission measurements were prepared by smearing the powders on the quartz plate with a spatula. Raman spectra were collected on a LabRAM HR Evolution Raman spectrometer (Horiba) excited with 785 nm laser. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC with a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopy (SEM) was performed on a HITACHI SU8020 (operating at 3 kV). The crystals were placed on silica wafer and coated with gold for SEM measurements. X-ray diffraction patterns were obtained on Empyrean XRD equipped with graphite monochromatized Cu-Ka radiation $(\lambda = 1.5418 \text{ Å})$ employing a scanning rate of 0.00267 °/s in the 20 range of 5° to 40° and the samples were kept at room temperature during data collection. Single crystals of Z-

FPhNaOMe, *Z*-**FPhNaF** and *E*-**FPhNaF** were selected for single crystal X-ray diffraction analysis on a Rigaku RAXIS-RA PID diffractometer using graphitemonochromated MoK_{α} radiation ($\lambda = 0.71073$ Å), and the crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program. All the reagents were used without further purification.

Preparation of the crystals for the photomechanical effect investigations: The crystals of Z-HPhNaH, Z-HPhNaF, Z-FPhNaH, Z-ClPhNaH, Z-BrPhNaH, Z-FPhNaF, Z-BrPhNaF and Z-FPhNaOMe were prepared by slow evaporation from the solutions in DCM/petroleum ether (v/v = 1/3). The crystals of Z-ClPhNaF were obtained by sublimation of the powders at 170 °C.

Preparation of the crystal of *E*-**FPhNaF**: The powders of *Z*-**FPhNaF** was dissolved in DCM (ca. 4.0×10^{-3} M), follow by irradiation with 365 nm light for 5 h, *E*-**FPhNaF** was gained in a yield of 74% after purified via column chromatography (silica gel, dichloromethane/petroleum ether in V/V = 1/5). The crystal of *E*-**FPhNaF** was obtained by slow evaporation in the mixed solvent of ethyl acetate/petroleum ether (V/V = 1/3).

Investigations of the photomechanical effects: The crystals were placed on the glass substrates or stuck at the needle tip/the end of the glass substrates (the scale of the gridding on the glass substrate is 0.2 mm). The hand-held flashlight (365 nm, 16.7 mW/cm²; and 410 nm, 16.7 mW/cm²) was used as the light source to irradiate the crystals at a distance of ca. 2 cm. The photomechanical motions were observed using optical microscopy or by naked eyes, and recorded by Redmi note 7.

Investigations of the force-induced bending behaviors of the crystals of *Z*-**FPhNaF** and *Z*-**FPhNaOMe**: One end of the crystal was stuck on the needle tip, and the force was applied on the other end of the crystal by another needle. And then, the force was removed. The moving process was recorded by Redmi note 7.

Synthesis

The intermediate of (4-fluoro-1-naphthaldehyde) was synthesized according to the

reported method.¹ ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.35 (s, 1H), 9.24 (d, *J* = 8.8 Hz, 1H), 8.27 (dd, *J* = 8.0, 5.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.62 (dd, *J* = 10.4, 8.4 Hz, 1H) (Figure S51). ¹³C NMR (101 MHz, CDCl₃) δ 192.15, 162.77 (d, *J* = 264.8 Hz), 137.90 (d, *J* = 11.0 Hz), 132.46 (d, *J* = 5.9 Hz), 130.14, 128.15 (d, *J* = 3.9 Hz), 127.40 (d, *J* = 2.0 Hz), 124.97 (d, *J* = 2.4 Hz), 123.88 (d, *J* = 15.9 Hz), 121.03 (d, *J* = 6.6 Hz), 109.08 (d, *J* = 16.4 Hz) (Figure S52). FT-IR (KBr, cm⁻¹): 3078.4, 2875.0, 2749.8, 1691.8, 1674.5, 1628.4, 1596.1, 1577.3, 1510.6, 1467.1, 1434.5, 1415.7, 1394.2, 1382.5, 1323.9, 1271.1, 1236.3, 1217.4, 1166.0, 1139.3, 1065.1, 1047.3, 1018.7, 827.1, 793.5, 776.7, 757.1, 702.5, 626.7, 587.3, 550.1, 493.5. HRMS (m/z) [M+H]⁺ calcd for C₁₁H₇FO 175.0561, found: 175.0540 (Figure S53).

(Z)-3-(4-fluoronaphthalen-1-yl)-2-(4-fluorophenyl)acrylonitrile (Z-FPhNaF)²

Sodium hydroxide (0. 14 g, 3.4 mmol) was dissolved in ethanol (~30 mL) in a 100 mL round bottom flask. 4-Fluoro-1-naphthaldehyde (0.5 g, 2.87 mmol) was added subsequently. After that, 2-(4-fluorophenyl)acetonitrile (0.47 g, 3.4 mmol) in ethanol (10 mL) was added dropwise. After stirred for 4 h, the reaction mixture was poured into water (200 mL). The crude product was collected via filtration over a Buchner funnel, and then the filter cake was dissolved in dichloromethane. The precipitation was removed to obtain the dichloromethane solution. Subsequently, the saturated dichloromethane solution was poured into petroleum ether (4 times of V_{DCM}) affords the yellow solid (0.56 g, yield is 67%). Mp: 208.0–209.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.66 (s, 1H), 8.28 – 8.25 (m, 1H), 8.19 - 8.17 (m, 1H), 8.03 (dd, J = 7.6, 5.2 Hz, 1H), 7.98 - 7.94 (m, 2H), 7.78 - 7.947.74 (m, 2H), 7.53 (dd, J = 10.4, 8.0 Hz, 1H), 7.44 – 7.40 (m, 2H) (Figure S54). ¹³C NMR $(101 \text{ MHz}, \text{CDCl}_3) \delta 163.41 \text{ (d}, J = 251.5 \text{ Hz}), 160.10 \text{ (d}, J = 258.5 \text{ Hz}), 139.19, 133.03$ (d, J = 5.1 Hz), 130.26 (d, J = 3.3 Hz), 128.14, 128.05 (d, J = 2.2 Hz), 127.43 (d, J = 9.0 Hz)Hz), 127.20 (d, J = 4.6 Hz), 126.84 (d, J = 2.1 Hz), 123.86 (d, J = 16.8 Hz), 123.36 (d, J= 2.7 Hz), 121.59 (d, J = 5.7 Hz), 117.58, 116.31 (d, J = 22.1 Hz), 114.17, 109.50 (d, J = 22.1 Hz), 114.17, 109 20.8 Hz) (Figure S55). FT-IR (KBr, cm⁻¹): 3079.8, 3067.2, 3046.0, 2217.9, 1629.9, 1601.5, 1579.8, 1510.4, 1465.5, 1426.6, 1415.7, 1380.0, 1307.9, 1280.5, 1238.4, 1165.6, 1152.8, 1109.4, 1063.1, 1038.6, 1013.5, 894.5, 834.3, 785.4, 768.1, 757.9, 707.1, 614.3, 568.6,

550.8, 518.5, 471.6, 428.7. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₁F₂N 292.0940, found: 292.0928 (Figure S56).

(Z)-3-(naphthalen-1-yl)-2-phenylacrylonitrile (Z-HPhNaH)

The synthetic method for compound *Z*-**HPhNaH** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-phenylacetonitrile (0.72 g, 6.15 mmol) and 1naphthaldehyde (0.8 g, 5.12 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/4$). White solid of *Z*-**HPhNaH** (0.91 g) was obtained in a yield of 70 %. Mp: 115.0–117.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.75 (s, 1H), 8.20 – 8.16 (m, 1H), 8.11 – 8.00 (m, 3H), 7.93 – 7.91 (m, 2H), 7.69 – 7.50 (m, 6H) (Figure S57). ¹³C NMR (101 MHz, CDCl₃) δ 139.28, 133.13, 132.48, 130.51, 130.12, 129.73, 128.45, 128.13, 127.95, 126.02, 125.95, 125.41, 125.18, 124.52, 122.34, 116.69, 114.29 (Figure S58). FT-IR (KBr, cm⁻¹): 3050.0, 3023.4, 2923.6, 2218.3, 1595.1, 1510.4, 1497.3, 1448.5, 1351.6, 1248.2, 1169.6, 1077.5, 911.3, 890.7, 858.5, 803.0, 793.0, 781.0, 758.9, 742.3, 685.8, 597.3, 552.0, 523.4, 483.2, 465.3. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁3N 256.1128, found: 256.1104 (Figure S59).

(*Z*)-3-(4-fluoronaphthalen-1-yl)-2-phenylacrylonitrile (*Z*-**HPhNaF**)

The synthetic method for compound *Z*-**HPhNaF** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-phenylacetonitrile (0.65 g, 5.5 mmol) and 4-fluoro-1-naphthaldehyde (0.8 g, 4.59 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/5$). White solid of *Z*-**HPhNaF** (0.84 g) was obtained in a yield of 67 %. Mp: 173.0–175.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.69 (s, 1H), 8.27 – 8.25 (m, 1H), 8.20 – 8.17 (m, 1H), 8.04 (dd, *J* = 7.6, 5.2 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.77 – 7.75 (m, 2H), 7.59 – 7.49 (m, 4H) (Figure S60). ¹³C NMR (101 MHz, CDCl₃) δ 160.05 (d, *J* = 258.2 Hz), 139.33, 134.06, 133.08 (d, J = 4.8 Hz), 129.57, 129.22, 127.99, 127.47, 127.36 (d, *J* = 4.0 Hz), 126.80 (d, *J* = 2.0 Hz), 126.21, 123.85 (d, J = 16.5 Hz), 123.44 (d, J = 2.9 Hz), 121.55 (d, J = 5.7 Hz), 117.71, 115.26, 109.50 (d, J = 20.9 Hz) (Figure S61). FT-IR (KBr, cm⁻¹): 3061.4, 2923.1, 2217.8, 1630.7, 1601.7, 1581.3, 1511.5, 1499.9, 1465.8, 1449.3, 1425.4, 1394.1, 1380.6, 1342.6, 1279.5, 1250.6, 1222.6, 1160.1, 1150.0, 1059.7, 1038.5, 1007.1, 983.8, 890.2, 860.8, 827.1, 786.9, 767.1, 754.4, 709.0, 685.0, 551.1, 507.4, 465.7, 416.9. HRMS (m/z)

 $[M+H]^+$ calcd for C₁₉H₁₂FN 274.1034, found: 274.1016 (Figure S62).

(Z)-2-(4-fluorophenyl)-3-(naphthalen-1-yl)acrylonitrile (Z-**FPhNaH**)

The synthetic method for compound *Z*-**FPhNaH** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-(4-fluorophenyl)acetonitrile (0.50 g, 3.70 mmol) and 1-naphthaldehyde (0.48 g, 3.08 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/4$). Light yellow solid of *Z*-**FPhNaH** (0.69 g) was obtained in a yield of 82 %. Mp: 160.0–163.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.73 (s, 1H), 8.20 – 8.18 (m, 1H), 8.17 – 7.96 (m, 5H), 7.69 – 7.63 (m, 3H), 7.42 (t, *J* = 8.8 Hz, 2H) (Figure S63). ¹³C NMR (101 MHz, CDCl₃) δ 163.39 (d, *J* = 251.3 Hz), 140.20 (d, *J* = 2.0 Hz), 133.54, 131.52, 131.01, 130.89, 130.39 (d, *J* = 3.2 Hz), 129.04, 128.13 (d, *J* = 8.5 Hz), 127.06 (d, *J* = 1.7 Hz), 126.51, 125.57, 123.32, 117.62, 116.39, 116.17, 114.26 (Figure S64). FT-IR (KBr, cm⁻¹): 3045.2, 2216.6, 1604.8, 1509.1, 1414.4, 1372.2, 1352.6, 1307.5, 1282.1, 1234.6, 1161.0, 1107.4, 1012.1, 912.2, 891.0, 834.5, 811.2, 801.5, 792.7, 777.9, 759.9, 727.7, 639.2, 627.8, 583.9, 550.1, 523.5, 502.3, 444.4, 426.8. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₂FN 274.1034, found: 274.1026 (Figure S65).

(Z)-2-(4-chlorophenyl)-3-(naphthalen-1-yl)acrylonitrile (Z-ClPhNaH)

The synthetic method for compound *Z*-**CIPhNaH** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-(4-chlorophenyl)acetonitrile (0.93 g, 6.15 mmol) and 1-naphthaldehyde (0.8 g, 5.12 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/4$). Light yellow solid of *Z*-**CIPhNaH** (1.0 g) was obtained in a yield of 68 %. Mp: 182.0–185.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.79 (s, 1H), 8.19 (dt, *J* = 6.4, 3.2 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.11 – 8.00 (m, 2H), 7.96 – 7.92 (m, 2H), 7.68 – 7.62 (m, 5H) (Figure S66). ¹³C NMR (101 MHz, CDCl₃) δ 140.64, 135.55, 133.54, 132.69, 131.51, 131.05, 130.88, 129.40, 129.06, 127.48, 127.15, 127.11, 126.54, 125.57, 123.28, 117.44, 114.16 (Figure S67). FT-IR (KBr, cm⁻¹): 3047.9, 2217.6, 1595.8, 1577.1, 1510.1, 1493.5, 1407.7, 1350.6, 1306.5, 1164.2, 1246.5, 1139.7, 1121.2, 1011.6, 1097.9, 992.2, 893.2, 870.0, 829.0, 813.8,

803.7, 794.1, 779.0, 765.0, 752.0, 725.8, 606.3, 539.4, 519.8, 507.8, 491.5. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₂ClN 290.0738 (³⁵Cl) and 292.0709 (³⁷Cl), found: 290.0714 (³⁵Cl) and 292.0693 (³⁷Cl) (Figure S68).

(Z)-2-(4-chlorophenyl)-3-(4-fluoronaphthalen-1-yl)acrylonitrile (Z-CIPhNaF)

The synthetic method for compound Z-CIPhNaF was similar to that of compound Z-FPhNaF. It was synthesized from 2-(4-chlorophenyl)acetonitrile (0.52 g, 3.45 mmol) and 4-fluoro-1-naphthaldehyde (0.5 g, 2.87 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether (V_{DCM}/V_{PE}=1/4). Light yellow solid of Z-ClPhNaF (0.61 g) was obtained in a yield of 70 %. Mp: 170.0–172.0 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 8.73 (s, 1H), 8.27 (dt, J =6.4, 2 Hz, 1H), 8.20 – 8.16 (m, 1H), 8.05 (dd, J = 8.0, 5.6 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.77 – 7.75 (m, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.53 (dd, J = 10.4, 8.0 Hz, 1H) (Figure S69). ¹³C NMR (101 MHz, CDCl₃) δ 160.19 (d, J = 258.6 Hz), 139.61, 135.62, 133.03 (d, J = 5.1 Hz), 132.57, 129.43, 128.10, 127.53 (d, J = 9.1 Hz), 127.44, 127.07 (d, J = 4.8Hz), 126.88 (d, J = 2.2 Hz), 123.86 (d, J = 16.6 Hz), 123.32 (d, J = 2.8 Hz), 121.61 (d, J= 5.6 Hz), 117.40, 114.05, 109.52 (d, J = 20.9 Hz) (Figure S70). FT-IR (KBr, cm⁻¹): 3059.5, 3048.4, 3037.8, 2216.9, 1630.9, 1600.4, 1576.9, 1513.5, 1493.4, 1465.7, 1426.7, 1408.1, 1378.2, 1344.6, 1305.9, 1273.9, 1252.1, 1224.6, 1155.7, 1097.9, 1061.1, 1012.7, 988.9, 893.8, 8303.6, 807.7, 787.2, 768.3, 756.0, 717.4, 551.7, 512.1, 486.4, 469.4, 419.6. HRMS (m/z) $[M+H]^+$ calcd for C₁₉H₁₁ClFN 308.0644 (³⁵Cl) and 310.0615 (³⁷Cl), found: 308.0626 (³⁵Cl) and 310.0597 (³⁷Cl) (Figure S71).

(*Z*)-2-(4-bromophenyl)-3-(naphthalen-1-yl)acrylonitrile (*Z*-**BrPhNaH**)

The synthetic method for compound *Z*-**BrPhNaH** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-(4-bromophenyl)acetonitrile (0.6 g, 3.06 mmol) and 1-naphthaldehyde (0.4 g, 2.55 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/5$). Yellow solid of *Z*-**BrPhNaH** (0.57 g) was obtained in a yield of 67 %. Mp: 189.0–191.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.80 (s, 1H), 8.18 (dt, *J* = 10.0, 3.2 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.11 – 8.00 (m, 2H), 7.88 – 7.85 (m, 2H), 7.78 – 7.76 (m, 2H), 7.68 – 7.62

(m, 3H) (Figure S72). ¹³C NMR (101 MHz, CDCl₃) δ 140.70, 133.54, 133.16, 132.36, 131.49, 131.08, 130.87, 129.06, 127.71, 127.14, 127.12, 126.55, 125.57, 123.74, 123.27, 117.37, 114.22 (Figure S73). FT-IR (KBr, cm⁻¹): 3058.5, 3047, 3035.9, 2216.6, 1595.1, 1509.5, 1487.5, 1403.6, 1349.4, 1244.8, 1164.3, 1139.1, 1121.3, 1077.0, 1008.1, 989.3, 892.5, 826.5, 814.7, 803.3, 794.0, 778.8, 762.6, 746.9, 725.4, 602.7, 548.3, 525.3, 502.9, 488.6. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₂BrN 334.0233 (⁷⁹Br) and 336.0213 (⁸¹Br), found: 334.0221 (⁷⁹Br) and 336.0199 (⁸¹Br) (Figure S74).

(Z)-2-(4-bromophenyl)-3-(4-fluoronaphthalen-1-yl)acrylonitrile (Z-**BrPhNaF**)

The synthetic method for compound Z-BrPhNaF was similar to that of compound Z-FPhNaF. It was synthesized from 2-(4-bromophenyl)acetonitrile (0.41 g, 2.1 mmol) and 4-fluoro-1-naphthaldehyde (0.3 g, 1.72 mmol). The crude product was purified by reprecipitation of the saturated dichloromethane solution in petroleum ether (V_{DCM}/V_{PE}=1/4). Yellow solid of Z-BrPhNaF (0.37 g) was obtained in a yield of 61 %. Mp: 162.0–164.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.74 (s, 1H), 8.27 – 8.25 (m, 1H), 8.18 - 8.16 (m, 1H), 8.04 (dd, J = 8.0, 5.6 Hz, 1H), 7.87 - 7.85 (m, 2H), 7.78 - 7.74 (m, 4H), 7.53 (dd, J = 10.4, 8.4 Hz, 1H) (Figure S75). ¹³C NMR (101 MHz, CDCl₃) δ 160.20 (d, J = 258.7 Hz), 139.66, 133.01 (d, J = 3.7 Hz), 132.38, 128.11, 127.67, 127.53 (d, J = 3.7 Hz), 132.11, 127.53 (d, J9.0 Hz), 127.06 (d, J = 4.6 Hz), 126.89 (d, J = 2.1 Hz), 123.95, 123.81, 123.31 (d, J = 2.7 Hz), 121.61 (d, J = 5.6 Hz), 117.34, 114.10, 109.63, 109.42 (Figure S76). FT-IR (KBr, cm⁻¹): 3726.2, 3701.1, 3440.7, 3065.9, 2923.3, 2217.4, 1631.0, 1600.7, 1589.9, 1513.3, 1488.6, 1466.2, 1426.3, 1403.4, 1378.7, 1344.4, 1271.3, 1250.9, 1224.2, 1153.4, 1077.9, 1061.2, 1010.7, 986.4, 960.7, 895.3, 832.4, 825.5, 806.4, 787.3, 768.5, 753.7, 731.3, 711.7, 673.8, 655.2, 634.3, 616.1, 551.4, 509.9, 484.5, 469.4, 417.8. HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₁BrFN 352.0139 (⁷⁹Br) and 354.0118 (⁸¹Br), found: 352.0131 (⁷⁹Br) and 354.0094 (⁸¹Br) (Figure S77).

(*Z*)-2-(4-fluorophenyl)-3-(4-methoxynaphthalen-1-yl)acrylonitrile (*Z*-**FPhNaOMe**)

The synthetic method for compound *Z*-**FPhNaOMe** was similar to that of compound *Z*-**FPhNaF**. It was synthesized from 2-(4-fluorophenyl)acetonitrile (0.35 g, 2.58 mmol) and 4-methoxy-1-naphthaldehyde (0.4 g, 2.15 mmol). The crude product was purified by

reprecipitation of the saturated dichloromethane solution in petroleum ether ($V_{DCM}/V_{PE}=1/4$). Yellow solid of *Z*-**FPhNaOMe** (0.43 g) was obtained in a yield of 66 %. Mp: 168.0–170.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.61 (s, 1H), 8.28 – 8.26 (m, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.69 – 7.61 (m, 2H), 7.40 (t, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H) (Figure S78). ¹³C NMR (101 MHz, CDCl₃) δ 163.14 (d, *J* = 250.7 Hz), 157.64, 140.04 (d, *J* = 2.0 Hz), 132.66, 130.83 (d, *J* = 3.4 Hz), 128.06, 127.91 (d, *J* = 8.3 Hz), 127.60, 125.81, 125.59, 123.34, 122.96 (d, *J* = 6.8 Hz), 118.30, 116.28, 116.06, 111.62, 103.58, 55.78 (Figure S79). FT-IR (KBr, cm⁻¹): 3077.4, 3008.7, 2972.3, 2947.5, 2894.2, 2481.9, 2215.2, 1620.8, 1587.1, 1579.2, 1509.0, 1465.7, 1415.0, 1381.0, 1343.5, 1308.3, 1288.3, 1257.6, 1232.4, 1162.3, 1098.6, 1030.2, 972.5, 894.5, 859.8, 835.2, 816.3, 803.6, 771.6, 752.9, 713.8, 615.5, 594.6, 518.6, 492.2, 473.1, 427.2. HRMS (m/z) [M+H]⁺ calcd for C₂₀H₁₄FNO 304.1139, found: 304.1124 (Figure S80).

Table S1 Interaction Energies (kJ/mol) obtained from energy framework calculation for*Z*-FPhNaF.

Interaction Energies (kJ/mol)

R is the distance between molecular centroids (mean atomic position) in \tilde{A}_{\cdot}

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

| | _ | _ | | | | | _ | _ |
|---|------------------|-------|------------------|-------|-------|-------|-------|-------|
| N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot |
| 2 | x+1/2, -y, z | 13.27 | B3LYP/6-31G(d,p) | -4.0 | -0.6 | -10.8 | 7.7 | -9.2 |
| 2 | x+1/2, -y, z | 13.37 | B3LYP/6-31G(d,p) | -0.6 | -0.2 | -6.7 | 2.1 | -5.3 |
| 2 | x, y, z | 3.84 | B3LYP/6-31G(d,p) | -6.0 | -2.0 | -96.1 | 58.9 | -55.2 |
| 2 | -x+1/2, y, z+1/2 | 8.10 | B3LYP/6-31G(d,p) | -12.9 | -3.7 | -16.8 | 16.1 | -21.1 |
| 2 | -x, -y, z+1/2 | 12.57 | B3LYP/6-31G(d,p) | 0.3 | -0.3 | -6.6 | 2.3 | -4.2 |
| 2 | -x+1/2, y, z+1/2 | 7.13 | B3LYP/6-31G(d,p) | -9.8 | -3.9 | -26.1 | 18.6 | -24.5 |
| 2 | -x+1/2, y, z+1/2 | 8.10 | B3LYP/6-31G(d,p) | -0.1 | -0.6 | -10.9 | 6.7 | -6.0 |
| 2 | -x, -y, z+1/2 | 13.60 | B3LYP/6-31G(d,p) | -0.9 | -0.2 | -2.9 | 0.5 | -3.2 |

See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_di sp | k_rep |
|---|-------|-------|---------|-------|
| CE-HF HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| $\mbox{CE-B3LYP}$ B3LYP/6-31G(d,p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

Scale factors for benchmarked energy models

Table S2 Interaction Energies (kJ/mol) obtained from energy framework calculation for

Z-FPhNaOMe.

Interaction Energies (kJ/mol)

R is the distance between molecular centroids (mean atomic position) in Ä.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

| N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|-------------------|--------|-------------------|-------|-------|-------|-------|--------|
| 2 | х, у, г | 3.87 | B3LYP/6-31G(d, p) | -3.2 | -3.0 | -98.9 | 55.6 | -57.4 |
| 2 | x, -y+1/2, z+1/2 | 8.14 | B3LYP/6-31G(d,p) | -14.1 | -4.1 | -15.9 | 13.5 | -23, 4 |
| 2 | -x, y+1/2, -z+1/2 | 15.04 | B3LYP/6-31G(d,p) | -2.6 | -0.4 | -5.6 | 2.6 | -6.4 |
| 2 | x, -y+1/2, z+1/2 | 8.23 | B3LYP/6-31G(d, p) | -0.9 | -0.4 | -10.6 | 5.7 | -7.0 |
| 2 | x, -y+1/2, z+1/2 | 7.21 | B3LYP/6-31G(d, p) | -11.9 | -4.3 | -31.8 | 22.7 | -29.4 |
| 1 | -x, -y, -z | 12.14 | B3LYP/6-31G(d, p) | -1.5 | -0.3 | -17.1 | 8.8 | -11.3 |
| 2 | -x, y+1/2, -z+1/2 | 14.88 | B3LYP/6-31G(d, p) | -0.5 | -0.3 | -4.4 | 2.2 | -3.3 |
| 1 | -x, -y, -z | 15. 18 | B3LYP/6-31G(d, p) | 1.4 | -0.3 | -1.8 | 0.1 | -0.3 |
| 1 | -x, -y, -z | 13.17 | B3LYP/6-31G(d, p) | -0.9 | -0.2 | -9.6 | 4.7 | -6.5 |

Scale factors for benchmarked energy models See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_di sp | k_rep |
|---|-------|-------|---------|-------|
| CE-HF HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| CE-B3LYP B3LYP/6-31G(d, p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

| | $a\lambda_{max}^{abs}/nm$ | ${}^b\lambda_{max}{}^{abs}/nm$ | ${}^b\lambda_{max}{}^{em}/nm$ | E _{HOMO} /eV | E _{LUMO} /eV | |
|-----------------------|---------------------------|--------------------------------|-------------------------------|-----------------------|-----------------------|--|
| (Z)-HPhNaH | 217, 337 | 207, 239, 341 | 469 | -5.83 | -2.13 | |
| (Z)-HPhNaF | 207, 224, 254, 334 | 207, 238, 338 | 478 | -5.94 | -2.25 | |
| (Z)-FPhNaH | 207, 254. 337 | 206, 236, 352 | 478 | -5.93 | -2.25 | |
| (Z)-FPhNaF | 208, 233, 337 | 205, 243, 346 | 483 | -6.04 | -2.38 | |
| (7) CIDhNaU | 209, 220, 256, 276, | 205 252 | 407 | 5 08 | 2 22 | |
| | 340 | 205, 555 | 497 | -3.98 | -2.33 | |
| (Z)-ClPhNaF | 207, 231, 275, 340 | 205, 239, 345 | 495 | -6.09 | -2.46 | |
| (7) DrDhNaII | 209, 220, 257, 277, | 208 252 | 400 | 5.04 | 2 21 | |
| (Z)- DIFFIINAR | 342 | 208, 555 | 490 | -3.94 | -2.31 | |
| (Z)-BrPhNaF | 207, 233, 275, 342 | 205, 240, 351 | 471 | -6.05 | -2.43 | |
| (Z)-FPhNaOMe | 207, 243, 361 | 205, 245, 361 | 511 | -5.59 | -2.09 | |

Table S3 The absorption and emission wavelengths, and the calculated HOMO andLUMO energy levels for 3-(naphthalen-1-yl)-2-phenylacrylonitrile derivatives.

^a in cyclohexane; ^b in powders. The HOMO and LUMO energy levels were calculated using Gaussian 09 calculations at the RB3LYP/6-31G(d) level.

| Compound | Conversion ratios (%) |
|------------|-----------------------|
| Z-HPhNaH | 11 |
| Z-HPhNaF | 26 |
| Z-FPhNaH | 7 |
| Z-FPhNaF | 12 |
| Z-ClPhNaH | 14 |
| Z-ClPhNaF | 10 |
| Z-BrPhNaH | 12 |
| Z-BrPhNaF | 17 |
| Z-FPhNaOMe | 30 |

Table S4 The conversion of photoisomerization of the 3-(naphthalen-1-yl)-2phenylacrylonitrile derivatives in the solid states after irradiation with 365 nm light for 30 min.

| | Z-FPhNaF | E-FPhNaF | Z-FPhNaOMe |
|----------------------------|--------------------|--------------------|-------------------------------------|
| Formula | $C_{19}H_{11}F_2N$ | $C_{19}H_{11}F_2N$ | C ₂₀ H ₁₄ FNO |
| Formula weight | 291.29 | 291.29 | 303.32 |
| Space group | $Pca2_1$ | $P2_1/c$ | $P2_1/c$ |
| Crystal system | orthorhombic | monoclinic | monoclinic |
| a/Å | 26.343(3) | 8.0153(2) | 3.8720(3) |
| b/Å | 3.8422(4) | 21.7501(6) | 28.953(2) |
| c/Å | 13.2780(17) | 8.4639(3) | 13.1938(11) |
| a/deg | 90 | 90 | 90 |
| β/deg | 90 | 96.220(1) | 90.852(3) |
| γ/deg | 90 | 90 | 90 |
| Volume/ Å ³ | 1343.9(3) | 1466.86(8) | 1479.0(2) |
| Z | 4 | 4 | 4 |
| D(calc)/g cm ⁻³ | 1.440 | 1.319 | 1.3622 |
| μ/mm^{-1} | 0.104 | 0.095 | 0.093 |
| Final R indexes | $R_1 = 0.0732$ | $R_1 = 0.0456$ | $R_1 = 0.0564$ |
| [I>2sigma(I)] | $wR_2 = 0.1507$ | $wR_2 = 0.1123$ | $wR_2 = 0.1238$ |
| R indexes (all data) | $R_1 = 0.0966$ | $R_1 = 0.0837$ | $R_1 = 0.0995$ |
| | $wR_2 = 0.1599$ | $wR_2 = 0.1439$ | $wR_2 = 0.1519$ |
| GoF | 1.117 | 1.038 | 1.031 |
| CCDC | 2101699 | 2101680 | 2101707 |

| | Z-FPhNaF | | E-FPh | NaF |
|------------------|-----------------|------------|-----------------|------------|
| Irradiation time | Retention times | content 0/ | Retention times | content 0/ |
| (s) | (min) | content % | (min) | content % |
| 0 | 37.623 | 100.0 | | 0.0 |
| 20 | 37.369 | 97.2 | 36.835 | 2.8 |
| 60 | 37.618 | 92.3 | 37.104 | 7.7 |
| 120 | 37.526 | 90.8 | 36.960 | 9.2 |
| 240 | 37.667 | 90.5 | 37.100 | 9.5 |
| 420 | 37.481 | 90.7 | 36.961 | 9.3 |
| 600 | 37.664 | 90.7 | 37.104 | 9.3 |

Table S6 HPLC data and the contents of *Z*-**FPhNaF** and *Z*-**FPhNaF** before and after irradiation of the crystals of *Z*-**FPhNaF** with 365 nm light (16.7 mW/cm²) for different times.



Figure S1 Normalized UV-vis absorption and fluorescence emission spectra of 3-(naphthalen-1-yl)-2-phenylacrylonitrile derivatives in cyclohexane (1.0×10^{-5} M, A and B, $\lambda_{ex} = 310$ nm) and in powders (C and D, $\lambda_{ex} = 370$ nm).



Figure S2 UV-vis absorption (A) and fluorescence emission (B, $\lambda_{ex} = 300$ nm) spectra of *Z*-FPhNaF in cyclohexane (1.0 × 10⁻⁵ M) before and after irradiation by 365 nm light (16.7 mW/cm²) for different times.



Figure S3 Fluorescence emission spectra of *Z*-FPhNaF and *E*-FPhNaF in cyclohexane $(1.0 \times 10^{-5} \text{ M}, \lambda_{ex} = 300 \text{ nm}).$



Figure S4 Microscopy images of the slice-like crystal of *Z***-FPhNaF** (504.2 μ m × 120.5 μ m × 0.7 μ m) upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation direction).



Figure S5 SEM images of cross-sections of the crystals in different sizes. The thickness of the crystals is in the range of $0.5-10 \ \mu m$.



Figure S6 ¹H NMR spectra of *Z*-**FPhNaF** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 5 s (ii) and 2 min (iii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S7 ¹H NMR spectra of *Z*-**FPhNaOMe** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 1 min (ii), 5 min (iii) and 10 min (iv) in DMSO- d_6 . The blue dots and rhombic boxes show the newly emerged signals after *Z*-*E* isomerism.



Figure S8 ¹H NMR spectra of *Z*-**FPhNaOMe** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 s (ii), 1 min (iii) and 5 min (iv) in microcrystals, followed by dissolved in DMSO- d_6 . The blue dots and boxes show the newly emerged signals after *Z*-*E* isomerism.



Figure S9 ¹H NMR spectrum of *Z*-**HPhNaH** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S10 ¹H NMR spectrum of *Z*-**HPhNaF** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S11 ¹H NMR spectrum of *Z*-**FPhNaH** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S12 ¹H NMR spectrum of *Z*-**CIPhNaH** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S13 ¹H NMR spectrum of *Z*-**ClPhNaF** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S14 ¹H NMR spectrum of *Z***-BrPhNaH** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO-*d*₆.



Figure S15 ¹H NMR spectrum of *Z*-**BrPhNaF** before (i) and after irradiation by 365 nm light (16.7 mW/cm²) for 30 min (ii) in microcrystals, followed by dissolved in DMSO- d_6 .



Figure S16 Raman spectra of the powder of *Z***-FPhNaF** before (blue) and after irradiation with 365 nm light for 30 s (green), 60 s (red) and 120 s (black).



Figure S17 HPLC spectra before and after irradiation of the crystals of *Z*-**FPhNaF** with 365 nm light (16.7 mW/cm²) for different times, UV chromatogram: 320-340 nm.



Figure S18 The relative content of the *Z*-**FPhNaF** and *E*-**FPhNaF** after irradiating the crystals of *Z*-**FPhNaF** with 365 nm light (16.7 mW/cm²) for different times.



Figure S19 The reaction cavity of approximately 357.08 Å³ in an asymmetric unit (viewed along b-axis) of *Z*-**FPhNaF** as mapped by the contact surface (yellow) of a probe with a radius of 0.3 Å.⁴⁻⁵



Figure S20 The reaction cavity of approximately 429.35 Å³ in an asymmetric unit (viewed along a-axis) of *Z*-**FPhNaOMe** as mapped by the contact surface (yellow) of a probe with a radius of 0.3 Å.⁴⁻⁵



Figure S21 Calculated growth morphology of *Z***-FPhNaF** in single crystal (A, B) viewed from the different crystallographic axis and microscopic images showing the widest face (C).



Figure S22 (A) The photoisomerization of *Z*-**FPhNaF** and the energy of the internal energy between the two isomers which is obtained by Gaussian simulation. Geometrical structures and the molecular size of *Z*-**FPhNaF** (B) and *E*-**FPhNaF** (C) in single crystals.



Figure S23 Thermal imaging photographs of the crystals of *Z***-FPhNaF** exposed to 365 nm light (16.7 mW/cm²) for different times.



Figure S24 DSC curves of *Z***-FPhNaF** measured at heating and cooling rate of 10 °C/min under a nitrogen atmosphere.



Figure S25 ¹H NMR spectra of *Z*-**FPhNaF** before (i) and after irradiation by 410 nm light (16.7 mW/cm²) for 45 min (ii) and 75 min (iii) in microcrystals, followed by dissolved in DMSO-*d*6, and ¹H-NMR spectrum of *E*-**FPhNaF** (iv). The blue dots and boxes show the newly emerged signals after *Z*-*E* isomerism.



Figure S26 Photographs during the bending and unbending of the slice-like crystal (4.100 \times 1.200 \times 0.007 mm³) of *Z*-**FPhNaF** upon irradiation by 410 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation direction, and one end of the crystal was stuck on a needle tip).



Figure S27 UV-vis absorption (A) and fluorescence emission (B, $\lambda_{ex} = 397$ nm) spectra of *Z*-**FPhNaOMe** in the microcrystals before and after irradiation by 365 nm light (16.7 mW/cm²) for different times.



Figure S28 Photographs during the bending and unbending of the needle-like crystal of *Z*-**FPhNaOMe** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation direction). The end of the crystal was stuck on a needle tip.



Figure S29 Photographs during the bending and unbending of the needle-like crystal of *Z*-**FPhNaOMe** upon irradiation by 410 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation direction). The end of the crystal was stuck on a needle tip.



Figure S30 changes of the bending angles of the crystal of *Z***-FPhNaF** during the bendingunbending cycle. A positive bending angle means that the light source is on the right and the crystal is bent to the left. A negative bending angle is the opposite.



Figure S31 Microscopy images of the slice-like crystal (2038.0 μ m × 293.3 μ m × 7.1 μ m) of *Z*-**FPhNaF** upon irradiation by 365 nm light (55.7 mW/cm²) for different times (the blue arrows indicate the irradiation direction).



Figure S32 Microscopy images of the elastic bending behaviors of the crystal of Z-FPhNaF.



Figure S33 2D fingerprint plots (A) and the Hirshfeld surface of an individual molecule in *Z*-**FPhNaF** (B); (C) relative contributions to the Hirshfeld surface of various contacts in the crystal of *Z*-**FPhNaF**.



Figure S34 Colour coding for the neighboring molecules around *Z*-**FPhNaF** (A) and *Z*-**FPhNaOMe** (B). The value of interaction energies between neighboring molecules can be seen in Tables S1-S2.



Figure S35 Calculated growth morphology of *Z*-**FPhNaOMe** in single crystal (A, B) viewed from the different crystallographic axis and microscopic images showing the widest face (C).


Figure S36 Molecular configuration (A) and molecular packing in the single crystals of *Z*-**FPhNaOMe** viewed along a-axis (B) and c-axis (C). The distance of H-bonds and the distance between the center (the red balls) of the adjacent aryl ring were given.



Figure S37 Energy frameworks corresponding to the coulomb (A, D), dispersion (B, E) and total interaction energy (C, F) components in crystals of *Z*-**FPhNaOMe** viewed from a-axis (left) and c-axis (right).



Figure S38 2D fingerprint plots (A), the Hirshfeld surface (B) of an individual molecule and relative contributions (C) to the Hirshfeld surface of various contacts in the crystal of *Z***-FPhNaOMe**.



Figure S39 (A) Elastic bending of a crystal of *Z*-**FPhNaOMe**. An end of the crystal was stuck on a needle, and another needle was used to apply pressure to the crystal. (B) Optical images of the needle-like crystal of *Z*-**FPhNaOMe** before and after irradiation by 365 nm light in water. The end of the crystal was stuck on a needle tip. The blue arrow represents the direction of irradiation and the white arrow represents the direction of crystal bending.



Figure S40 Optical microscope photos of the slice-like crystal of *Z*-**HPhNaH** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the dark blue–arrow indicate the irradiation directions, and one end of the crystal was stuck on the edge of glass slide).



Figure S41 Optical microscope photos of the ribbon-like crystal of *Z*-**HPhNaF** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions).



Figure S42 Optical microscope photos of the sheet-like crystal of *Z*-**FPhNaH** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions).



Figure S43 Optical microscope photos of the slice-like crystal of *Z*-**CIPhNaF** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions).



Figure S44 Optical microscope photos of the sheet-like crystal of *Z*-**ClPhNaH** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions).



Figure S45 Optical microscope photos of the needle-like crystal of *Z*-**BrPhNaH** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions).



Figure S46 Optical microscope photos of the needle-like crystal of *Z*-**BrPhNaF** upon irradiation by 365 nm light (16.7 mW/cm²) for different times (the blue arrows indicate the irradiation directions , and one end of the crystal was stuck on the edge of glass slide).



Figure S47 ¹H NMR spectra of *E*-**FPhNaF** in microcrystals before (i) and after irradiating with 365 nm (ii), 254 nm (iii) and 410 nm (iv) light for 30 min, 1 h and 1 h, respectively, followed by dissolved in DMSO- d_6 .



Figure S48 ¹H NMR spectrum of *E*-**FPhNaF** in solid state before (i) and after (ii) heating at 373 K for 30 min, followed by dissolved in DMSO- d_6 .



Figure S49 DSC curves of *E*-**FPhNaF** measured at heating and cooling rate of 10 °C/min under a nitrogen atmosphere.



Figure S50 ¹H NMR spectra of as-prepared *E*-**FPhNaF** (i) after heating at 140 °C for 20 h in DMSO- d_6 solution (ii) and sublimation of the powder (iii).



Figure S51 ¹H NMR (400 MHz) spectrum of 4-fluoro-1-naphthaldehyde in DMSO-*d*₆.



Figure S52 ¹³C NMR (101 MHz) spectrum of 4-fluoro-1-naphthaldehyde in CDCl₃.



Figure S53 The HRMS of 4-fluoro-1-naphthaldehyde.



Figure S54 ¹H NMR (400 MHz) spectrum of Z-FPhNaF in DMSO-d₆.



Figure S55 ¹³C NMR (101 MHz) spectrum of Z-FPhNaF in CDCl₃.



Figure S56 The HRMS of Z-FPhNaF.



Figure S57 ¹H NMR (400 MHz) spectrum of Z-HPhNaH in DMSO-d₆.



Figure S58 ¹³C NMR (101 MHz) spectrum of Z-HPhNaH in CDCl₃.



Figure S59 The HRMS spectrum of Z-HPhNaH.



Figure S60 ¹H NMR (400 MHz) spectrum of Z-HPhNaF in DMSO-d₆.



Figure S61 ¹³C NMR (101 MHz) spectrum of Z-HPhNaF in CDCl₃.



Figure S62 The HRMS of Z-HPhNaF.



Figure S63 ¹H NMR (400 MHz) spectrum of Z-FPhNaH in DMSO-d₆.



Figure S64 ¹³C NMR (101 MHz) spectrum of Z-FPhNaH in CDCl₃.



Figure S65 The HRMS of Z-FPhNaH.



Figure S66 ¹H NMR (400 MHz) spectrum of Z-ClPhNaH in DMSO-d₆.



Figure S67 ¹³C NMR (101 MHz) spectrum of Z-ClPhNaH in CDCl₃.



Figure S68 The HRMS of Z-ClPhNaH.



Figure S69 ¹H NMR (400 MHz) spectrum of Z-ClPhNaF in DMSO-d₆.



Figure S70 ¹³C NMR (101 MHz) spectrum of Z-ClPhNaF in CDCl₃.



Figure S71 The HRMS of Z-CIPhNaF.



Figure S72 ¹H NMR (400 MHz) spectrum of Z-BrPhNaH in DMSO-d₆.



Figure S73 ¹³C NMR (101 MHz) spectrum of Z-BrPhNaH in CDCl₃.



Figure S74 The HRMS of Z-BrPhNaH.



Figure S75 ¹H NMR (400 MHz) spectrum of Z-BrPhNaF in DMSO-d₆.



Figure S76¹³C NMR (101 MHz) spectrum of Z-BrPhNaF in CDCl₃.



Figure S77 The HRMS of Z-BrPhNaF.



Figure S78 ¹H NMR (400 MHz) spectrum of Z-FPhNaOMe in DMSO-d₆.



Figure S79¹³C NMR (101 MHz) spectrum of Z-FPhNaOMe in CDCl₃.



Figure S80 The HRMS of Z-FPhNaOMe.

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Structure factors have been supplied for datablock(s) Z-FPhNaF

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Z-FPhNaF

| C-C = 0.00 | 65 A | Wavelength=0.71073 | | | | |
|--------------|--|--|---|--|--|--|
| a=26.343(| 3) | b=3.8422(4) | C= | 13.2780(17) | | |
| alpha=90 | | beta=90 | ga | mma=90 | | |
| 100 K | | | | | | |
| Calculated | | Repo | orted | | | |
| 1343.9(3) | | 1343 | 3.9(3) | | | |
| P c a 21 | | Рс | a 21 | | | |
| P 2c -2ac | | P 20 | c -2ac | | | |
| C19 H11 F2 N | 1 | C19 | H11 F2 | N | | |
| C19 H11 F2 N | 1 | C19 | H11 F2 | N | | |
| 291.29 | | 291. | .29 | | | |
| 1.440 | | 1.44 | 40 | | | |
| 4 | | 4 | | | | |
| 0.104 | | 0.10 |)4 | | | |
| 600.0 | | 600. | . 0 | | | |
| 600.32 | | | | | | |
| 36,5,18 | | 36,5 | 5 , 18 | | | |
| 3819[1989] | | 3747 | 7 | | | |
| 0.986,0.990 | | | | | | |
| 0.986 | | | | | | |
| d= Not given | | | | | | |
| s= 1.88/0.98 | | Theta(max) = | 29.641 | | | |
| 0.0732(2971 |) | | | wR2(reflections)= | | |
| Ng | par= 199 | 1 | | 0.1000 0/11/ | | |
| | C-C = 0.00 a=26.343(alpha=90 100 K Calculated 1343.9(3) P c a 21 P 2c -2ac C19 H11 F2 M C19 H11 F2 M 291.29 1.440 4 0.104 600.0 600.32 36,5,18 3819[1989] 0.986,0.990 0.986 d= Not given s= 1.88/0.98 0.0732(2971 Ng | C-C = 0.0065 A a=26.343(3) alpha=90 100 K Calculated 1343.9(3) P c a 21 P 2c -2ac C19 H11 F2 N 291.29 1.440 4 0.104 600.0 600.32 36,5,18 3819[1989] 0.986,0.990 0.986 d= Not given s= 1.88/0.98 0.0732(2971) Npar= 199 | C-C = 0.0065 A Wavel a=26.343(3) $b=3.8422(4)$ $beta=90100 KCalculated Reported1343.9(3) 1342P c a 21 P cP 2c -2ac P 2cC19 H11 F2 N C19291.29 2911.440 4 40.104 0.104600.0 600600.3236,5,18 36,53819[1989] 3740.986,0.9900.986d= Not givens= 1.88/0.98 Theta(max)=0.0732(2971)Npar= 199$ | C-C = 0.0065 A Wavelength= a=26.343(3) b=3.8422(4) c= alpha=90 beta=90 ga 100 K Calculated Reported 1343.9(3) P c a 21 P c a 21 P 2c -2ac C 19 H11 F2 N C19 H11 F2 N C19 H11 F2 291.29 291.29 1.440 4 4 0.104 0.104 600.0 600.0 600.32 36,5,18 36,5,18 3819[1989] 3747 0.986,0.990 0.986 d= Not given s= 1.88/0.98 Theta(max)= 29.641 0.0732(2971) Npar= 199 | | |

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

| STRVA01_ALERT_4_C | Flack paramet | er is too small | | | |
|----------------------|------------------------|----------------------|-------|---------|--------|
| From the | CIF: _refine_ls_abs_s | structure_Flack -0. | 300 | | |
| From the | CIF: _refine_ls_abs_s | structure_Flack_su | 0.400 | | |
| PLAT213_ALERT_2_C At | om C4 ha | as ADP max/min Ratio | | 3.2 | oblate |
| PLAT340_ALERT_3_C Lc | w Bond Precision on | C-C Bonds | | 0.00648 | Ang. |
| PLAT906_ALERT_3_C La | arge K Value in the Ar | alysis of Variance . | | 3.409 | Check |

Alert level G

| PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High . | 0.400 | Report |
|---|-------|--------|
| PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). | 2 | Note |
| PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 | 16 | Note |
| <code>PLAT916_ALERT_2_G</code> Hooft y and <code>Flack</code> x <code>Parameter</code> Values Differ by . | 0.10 | Check |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 15 | Info |

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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PLATON version of 18/05/2022; check.def file version of 17/05/2022

Datablock Z-FPhNaF - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) E-FPhNaF

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: E-FPhNaF

| Bond precision: | C-C = 0.0027 A | Wavelength= | 0.71073 | | | |
|------------------|-------------------------|--------------------------------|---|--|--|--|
| Cell: | a=8.0153(2) alpha=90 | b=21.7501(6) beta=96.220(1) | c=8.4639(3) gamma=90 | | | |
| Temperature: | 110 K | | 5 | | | |
| | Calculated | Reported | | | | |
| Volume | 1466.86(8) | 1466.86(8) | | | | |
| Space group | P 21/c | P 1 21/c 1 | | | | |
| Hall group | -P 2ybc | -P 2ybc | | | | |
| Moiety formula | C19 H11 F2 N | C19 H11 F2 | N | | | |
| Sum formula | C19 H11 F2 N | C19 H11 F2 | N | | | |
| Mr | 291.29 | 291.29 | | | | |
| Dx,g cm-3 | 1.319 | 1.319 | | | | |
| Z | 4 | 4 | | | | |
| Mu (mm-1) | 0.095 | 0.095 | | | | |
| F000 | 600.0 | 600.0 | | | | |
| F000′ | 600.32 | | | | | |
| h,k,lmax | 10,28,10 | 10,28,10 | | | | |
| Nref | 3369 | 3363 | | | | |
| Tmin,Tmax | 0.994,0.995 | | | | | |
| Tmin' | 0.991 | | | | | |
| Correction metho | od= Not given | | | | | |
| Data completenes | ss= 0.998 | Theta(max) = 27.490 | | | | |
| R(reflections)= | 0.0456(2032) | | <pre>wR2(reflections) = 0.1439(3363)</pre> | | | |
| S = 1.038 | Npar= 1 | 200 | 0.1109(0000) | | | |

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

| PLAT242_ALERT_2_C Lo | ow 'MainMol' | Ueq as | Compared | to Neighbors | of | C1 Check |
|----------------------|-----------------|---------|-----------|---------------|-----|---------------|
| PLAT905_ALERT_3_C Ne | egative K value | in the | Analysis | of Variance . | •• | -7.672 Report |
| PLAT905_ALERT_3_C Ne | egative K value | in the | Analysis | of Variance . | •• | -0.213 Report |
| PLAT911_ALERT_3_C M: | issing FCF Refl | Betweer | n Thmin & | STh/L= 0.6 | 500 | 4 Report |

Alert level G

| PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). | 1 | Note |
|--|---|-------|
| PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 | 1 | Note |
| PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF | 3 | Note |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 0 | Info |
| PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by | 2 | Check |

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PLATON version of 18/05/2022; check.def file version of 17/05/2022

Datablock E-FPhNaF - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) Z-FPhNaOMe

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Z-FPhNaOMe

| Bond precision: | C-C = 0.0033 A | Wavel | ength=0.71073 |
|------------------|----------------|----------------|-------------------|
| Cell: | a=3.8720(3) | b=28.953(2) | c=13.1938(11) |
| | alpha=90 | beta=90.852(3) | gamma=90 |
| Temperature: | 100 K | | |
| | Calculated | Repo | rted |
| Volume | 1478.9(2) | 1479 | .0(2) |
| Space group | P 21/c | P 1 | 21/c 1 |
| Hall group | -P 2ybc | -P 2 | уbс |
| Moiety formula | C20 H14 F N O | C20 | H14 F N O |
| Sum formula | C20 H14 F N O | C20 | H14 F N O |
| Mr | 303.32 | 303. | 32 |
| Dx,g cm-3 | 1.362 | 1.36 | 2 |
| Z | 4 | 4 | |
| Mu (mm-1) | 0.093 | 0.09 | 3 |
| F000 | 632.0 | 632. | 0 |
| F000′ | 632.31 | | |
| h,k,lmax | 5,37,17 | 5 , 37 | ,17 |
| Nref | 3363 | 3355 | |
| Tmin,Tmax | 0.987,0.992 | | |
| Tmin' | 0.968 | | |
| Correction metho | od= Not given | | |
| Data completenes | ss= 0.998 | Theta(max) = | 27.491 |
| R(reflections)= | 0.0577(2234) | | wR2(reflections)= |
| S = 1.025 | Npar= | 203 | 0.1303(3333) |

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Click on the hyperlinks for more details of the test.

➔ Alert level C

| PLAT094_ | _ALERT_ | _2_C | Ratio of | Ma | aximum | / | Minim | um Res: | dual | Density | 2.36 | Report |
|----------|---------|------|----------|----|--------|----|-------|---------|------|----------|------------|--------|
| PLAT905_ | _ALERT_ | _3_C | Negative | Κ | value | in | the | Analys | s of | Variance | -2.178 | Report |

Alert level G

| PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite | 3 Note |
|--|----------|
| PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records | 1 Report |
| PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records | 1 Report |
| PLAT860_ALERT_3_G Number of Least-Squares Restraints | 1 Note |
| PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). | 3 Note |
| PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 | 5 Note |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 8 Info |

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Datablock Z-FPhNaOMe - ellipsoid plot

