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## Supporting Information

for

# Spiropyran-Based Multi-Colored Switch Tuned by Pressure and Mechanical Grinding

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#### **1. Experimental Section**

**General Methods**: Chemicals were purchased commercially and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from sodium under N<sub>2</sub> prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker-400 (400 MHz) spectrometer using CDCl<sub>3</sub> as solvent. Chemical shifts are reported in parts per million (ppm). <sup>1</sup>H NMR chemical shifts were referenced versus TMS (0 ppm), while <sup>13</sup>C NMR chemical shifts were referenced versus CDCl<sub>3</sub> (77.0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Differential scanning calorimetry (DSC) experiments were measured on DSC Q100 (Thermal Analysis) under N<sub>2</sub> atmosphere with scanning rate of 1 °C min<sup>-1</sup> from 0 to 200 °C for samples. Powder X-ray diffraction (PXRD) data was collected on a PHILIPS X'Pert Pro diffractometer with an X'celerator detector in the reflection mode, using monochromatized Cu Kα radiation.

High pressure experiments were performed using symmetric diamond anvil cells (DACs) at room temperature. The culet diameter of the diamond anvils was 500  $\mu$  m.

The crystal was placed in the holes (diameter: ca. 170 µm) of a T301 steel gasket,

which was pre-indented to a thickness of 50 µ m. The silicon oil was used as pressure transmitting medium (PTM). A small ruby chip was inserted into the sample compartment for in situ pressure calibration according to the R1 ruby fluorescence method. The photoluminescence measurements under high pressure were performed on a QE65000 Scientific-grade spectrometer in the reflection mode. The 355 nm line of a laser with a power of 10 mW was used as the excitation source. The in situ UV-Vis absorption measurements under high pressure are performed on an Ocean Optics QE65000 Scientific-grade spectrometer. The images of the powder under visible light and 365 nm UV light with a power of 75 W were taken by putting the DAC containing the sample on a Nikon fluorescence microscope.



Scheme S1. General procedure for the synthesis of SP-Pyr.

**1',3',3'-Trimethyl-7-(pyren-1-yl)spiro[chromene-2,2'-indoline](SP-Pyr):** A 100 mL Schlenk tube was charged with **1** (synthesized according to the previous literature<sup>[1]</sup>) (0.520 g, 1.46 mmol), **2** (0.400 g, 1.1 eq per C-Br bond),  $Pd(PPh_3)_2Cl_2$  (0.066 g, 6% mol per C-Br bond),  $Na_2CO_3$  (0.928 g, 8.76 mmol). The tube was evacuated and back-filled with nitrogen 3 times. Degassed H<sub>2</sub>O (3 mL) and THF (10 mL) were added to the mixture under nitrogen atmosphere. The mixture was stirred under reflux overnight. The aqueous layer was then extracted with ethyl acetate (EtOAc). The combined organic layers were washed with water and brine, dried over anhydrous  $Na_2SO_4$ , filtered and concentrated in vacuum. The solid residue was subjected to column chromatography (silica gel, PE/EtOAc=100:1) to get the product as a white powder.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (d, *J*= 9.3 Hz, 1H), 8.19-8.14 (m, 3H), 8.07 (s, 2H), 8.01-7.98 (m, 2H), 7.93 (d, *J*= 7.9 Hz, 1H), 7.23 (d, *J*= 7.6 Hz, 1H), 7.19-7.15 (m, 1H), 7.12-7.08 (m, 2H), 7.06 (s, 1H), 6.99 (d, *J*= 10.2 Hz, 1H), 6.85 (m, 1H), 6.55 (d, *J*= 7.7 Hz, 1H), 5.78 (d, *J*= 10.2 Hz 1H), 2.85 (s, 3H), 1.42 (s, 3H), 1.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.5, 148.2, 142.8, 136.8, 126.5, 125.1, 124.6, 119.7, 117.2, 106.8, 104.5, 51.9, 29.1, 25.9, 20.4; HR-MS (ESI) m/z: Calcd. for [(M+H)+]: 478.2165, Found 478.2158; Anal. Calcd. for C<sub>35</sub>H<sub>27</sub>NO: C: 88.02; N, 2.93; H, 5.70; Found: C, 87.80; N, 2.79; H, 5.83.

## 2. <sup>1</sup>H NMR, <sup>13</sup>C NMR Spectra



Figure S2-1. <sup>1</sup>H NMR spectrum of SP-Pyr in CDCl<sub>3</sub>.



*Figure S2-2.* <sup>13</sup>C NMR spectrum of **SP-Pyr** in CDCl<sub>3</sub>.

### 3. Mechanochromic Property Characterizations



*Figure S3-1.* Fluorescence spectrum ( $\lambda_{ex} = 365 \text{ nm}$ ) of the solution ( $c = 1 \times 10^{-5} \text{ mol/L}$ ) of **SP-Pyr** in toluene ( $\lambda_{max} = 400 \text{ nm}$ ).



*Figure S3-2.* The fluorescence spectra ( $\lambda_{ex} = 355$  nm) of **SP-Pyr** under pressure of 0-8.3 GPa without normalization during the compression process.



*Figure S3-3.* The normalized fluorescence spectra ( $\lambda_{ex} = 355$  nm) of **SP-Pyr** under pressure of 0-15.0 GPa. The emission intensity became weak over 10 GPa and the fluorescent interference (around 400-450 nm) from the diamond could be observed.



*Figure S3-4.* (a) In situ UV-Vis spectra of SP-Pyr under pressure in the range of 0-13.0 GPa. (b) The comparison of UV-Vis spectra of SP-Pyr powder before (0 GPa) and after (-0 GPa) the pressure treatment. (c) In situ micrographs of SP-Pyr powder during the compression and decompression process (0-13.0 GPa). (d) In situ micrographs of SP-Pyr powder during the compression and decompression and decompression process (0-8.3 GPa).



*Figure S3-5.* Time-resolved emission decay curves of the initial powder ( $\lambda_{max} = 424$  nm) and the sample after grinding ( $\lambda_{max} = 476$  nm) (excited at 369 nm with a nanoLED).



*Figure S3-6.* The PXRD patterns of the initial powder, the sample after light grinding, and the recovered sample of the lightly ground powder after hexane fuming.



*Figure S3-7.* DSC graphs of the initial powder (a) and ground powder (b) DSC measurement results indicated the amorphous nature of the ground sample through measuring its thermal property. An exothermic transition of the amorphous state was detected, indicating that the aggregation structure of the ground sample transformed from a metastable state into a more stable packing structure.<sup>[2]</sup>



*Figure S3-8.* Fluorescence spectra ( $\lambda_{ex} = 365 \text{ nm}$ ) of the initial powder, the sample after light grinding and the recovered sample of the lightly ground powder after hexane fuming.



Figure S3-9. UV-Vis absorption spectrum of the SP-Pyr powder after heavy grinding.



*Figure S3-10.* Fluorescence spectra ( $\lambda_{ex} = 365$  nm) of the initial powder, the sample after light grinding, the sample after heavy grinding and the recovered sample of the heavily ground powder after hexane fuming.

# **Reference:**

- [1] Q. Qi, J. Qian, S. Ma, B. Xu, S. X. A. Zhang and W. Tian, *Chem. Eur. J.*, 2015, 21, 1149-1155.
- [2] M. J. Teng, X. R. Jia, S. Yang, X. F. Chen and Y. Wei, Adv. Mater., 2012, 24, 1255-1261.