# Tailoring Effects of Chain Length and Terminal Substituent on the

# **Photochromism of Solid-state Spiropyrans**

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#### 1. General remarks

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 500 (500 and 125 MHz, respectively) with CDCl<sub>3</sub> as a solvent. Chemical shifts were determined relative to the residual solvent peaks (CHCl<sub>3</sub>,  $\delta$  = 7.26 ppm for <sup>1</sup>H NMR,  $\delta$  = 77.0 ppm for <sup>13</sup>C-NMR). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL machine. The UV-vis absorption spectra were recorded on a Shimadzu UV-2600 UV-vis spectrophotometer, and all the related studies were carried out on fast scan mode with slit widths of 1.0 nm, using matched quartz cells. SAXS was performed by employing a conventional X-ray source with radiation wavelength of  $\lambda$  = 1.54 Å. The sample holder is a metal plate with a small hole (diameter  $\approx$  0.5 cm, thickness  $\approx$  0.5 cm), where the X-ray beam passes through and the sample-to-detector distance was 20 cm. The scattering vector *q* is defined as *q* = 4 $\pi$  sin $\theta/\lambda$  with 2 $\theta$  being the scattering angle. All absorption scans were saved as ACS II files and further processed in OriginLab software to produce all graphs shown. The wavelengths of UV and vis photoirradiations are 365 nm (0.018 W cm<sup>-2</sup>) and 520 nm (0.068 W cm<sup>-2</sup>), respectively.

All starting materials, reagents and solvents were purchased and used without further purification. The solid-state  $SP_4$ -Br,  $SP_8$ -Br,  $SP_{12}$ -Br,  $SP_8$ -H and  $SP_8$ -I used for UV-Vis absorption spectra measurements were prepared by heating the corresponding powder sample to melted state and then cooling to room temperature for the attachment to the cell wall. One solely solid-state sample was used in both UV and vis absorption measurements. Following a similar operation on preparing samples for UV-Vis absorption, the solid samples used for the SAXS measurements were prepared by heating to the melted state and cooling to room temperature.

#### 2. Synthesis of SP<sub>4</sub>-Br, SP<sub>8</sub>-Br, SP<sub>12</sub>-Br, SP<sub>8</sub>-H and SP<sub>8</sub>-I

**General procedure for the one-pot synthesis of spiropyrans**: to a solution of 2,3,3-trimethyl-3*H*-indole (0.5 mL, 3.14 mmol) in EtOH (20 mL) was added halides (3.14mmol, 1 eq), respectively, and the resulting mixture was refluxed over 24 h. Then the reaction mixture was lowered down to the room temperature, which was followed by the addition of piperidine (0.31 mL, 3.14mmol, 1 eq) and 2-hydroxyl-5-nitrobenzaldehyde (3.14 mmol, 1 eq). The reaction was stirred over 5 min. Finally, the crude product was purified via a quick column chromatography to afford SP<sub>4</sub>-Br, SP<sub>8</sub>-Br, SP<sub>8</sub>-H and SP<sub>8</sub>-I as yellow solids.



**SP<sub>4</sub>-Br, SP<sub>8</sub>-Br, SP<sub>12</sub>-Br: SP<sub>4</sub>-Br, SP<sub>8</sub>-Br, SP<sub>12</sub>-Br** were obtained in 30~60% (an average number over several batches) yields, respectively, and <sup>1</sup>H NMR spectra coincided with those reported in our previous results.<sup>1, 2</sup>



SP<sub>8</sub>-H, SP<sub>8</sub>-I: SP<sub>8</sub>-H and SP<sub>8</sub>-I were obtained in 65% and 57% yields, respectively.

**SP<sub>8</sub>-H:** (known compound)<sup>3, 4 1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02-7.99 (m, 2 H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1 H), 6.90-6.84 (m, 2 H), 6.74 (d, *J* = 9.0 Hz, 1 H), 6.57 (d, *J* = 8.0 Hz, 1 H), 5.86 (d, *J* = 10.0 Hz, 1 H), 3.20-3.18 (m, 2 H), 1.64-1.52 (m, 2 H), 1.28-1.23 (m, 13 H), 1.18 (s, 3 H), 0.86 (t, *J* = 7.0 Hz, 3 H).

**SP**<sub>8</sub>-I: (new compound) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03-8.02 (m, 2 H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.0 Hz, 1 H), 6.93 (d, J = 10.5 Hz, 1 H), 6.88 (t, J = 7.5 Hz, 1 H), 6.75 (d, J = 10.0 Hz, 1 H), 6.58 (d, J = 8.0 Hz, 1 H), 5.89 (d, J = 10.5 Hz, 1 H), 4.23-3.12 (m, 4 H), 1.84-1.78 (m, 2 H), 1.67-1.57 (m, 2 H), 1.38-1.31 (m, 11 H), 1.21 (s, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.7, 147.2, 140.9, 136.0, 128.1, 127.8, 125.9, 122.7, 122.1, 121.7, 119.3, 118.6, 115.6, 106.8, 106.7, 52.7, 43.8, 33.5, 30.4, 29.2, 28.9, 28.5, 27.2, 26.1, 19.9, 7.3. HRMS (ESI) calcd. for C<sub>26</sub>H<sub>32</sub>IN<sub>2</sub>O<sub>3</sub> [M + H]<sup>-</sup> 547.1452, found 547.1466.



<sup>1</sup>H NMR of **SP<sub>8</sub>-H** 



<sup>1</sup>H NMR of **SP<sub>8</sub>-I** 



<sup>13</sup>C NMR of **SP<sub>8</sub>-I** 



HRMS of SP<sub>8</sub>-I

### 3. Characterizations of photochromism of solid-state spiropyrans



Figure S1. Pictures of photochromism of solid-state SP<sub>4</sub>-Br.







Figure S2. Pictures of photochromism of solid-state SP<sub>8</sub>-Br.



Figure S3. Pictures of photochromism of solid-state SP<sub>12</sub>-Br.



Figure S4. Pictures of photochromism of solid-state SP<sub>8</sub>-H.



Figure S5. Pictures of photochromism of solid-state SP<sub>8</sub>-I.



Figure S6. Time-dependent UV-Vis absorption spectral changes of SP<sub>4</sub>-Br.



Figure S7. Time-dependent UV-Vis absorption spectral changes of SP<sub>8</sub>-Br.



Figure S8. Time-dependent UV-Vis absorption spectral changes of SP<sub>12</sub>-Br.



Figure S9. Time-dependent UV-Vis absorption spectral changes of SP<sub>8</sub>-H.



Figure S10. Time-dependent UV-Vis absorption spectral changes of SP<sub>8</sub>-I.



Figure S11. The comparison on the <sup>1</sup>H NMR of SP<sub>8</sub>-Br before and after UV irradiation.



Figure S12. A comparison on the SAXS profiles of SP<sub>8</sub>-H, SP<sub>8</sub>-Br and SP<sub>8</sub>-I.

### References

- 1. L. Zhang, Y. Deng, Z. Tang, N. Zheng, C. Zhang, C. Xie and Z. Wu, A. J. Org. Chem., 2019, **8**, 1866-1869.
- 2. L. Zhang, Y. Deng, Y. Tang, C. Xie and Z. Wu, *Mater. Chem. Front.*, 2021, **5**, 3119-3124.
- 3. J. Warner, C. and S. Cheruku, R., *PCT Int. Appl.*, 2017, WO 2017/223413 Al 20171228.
- 4. J. G. S. Moo, S. Presolski and M. Pumera, *ACS Nano*, 2016, **10**, 3543-3552.