*Supplementary Materials*

# Synthesis and Properties of a Bay-Annulated-Indigo Tetramer Based on Low-Cost Spiro[Fluorene-9,9′-Xanthene] Core

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### *1. Cost estimations*

Cost estimations of 4Br-SFX and bromo-BAI were adapted from [1] and [2].

***Table S1***. *Material quantities and costs for the synthesis of 4Br-SFX.*

| Chemical name | Weight reagent (g/g) | Weight solvent (g/g) | Weight workup (g/g) | Price of Chemical ($/kg) | Material cost ($/g product) | Total cost ($/g) |
|---|---|---|---|---|---|---|
| 2,7-dibromo-9*H*-fluoren-9-one | 2.33 | | | 285 | 0.23 | 3.20 |
| 3-bromophenol | 11.92 | | | 150 | 0.60 | |
| $MeSO_3H$ | 3.98 | | | 60.5 | 0.08 | |
| EtOH | | | 50 | 5.8 | 0.22 | |
| Ethyl acetate | | | 40 | 3.4 | 0.20 | |
| petroleum ether | | | 240 | 2.9 | 0.54 | |
| Silica gel | | | 20 | 8.0 | 0.13 | |

***Table S2***. *Materials quantities and cost for the synthesis of bromo-BAI.*

| Chemical name | Weight reagent (g/g) | Weight solvent (g/g) | Weight workup (g/g) | Price of chemical ($/kg) | Material cost ($/g product) | Total cost ($/g) |
|---|---|---|---|---|---|---|
| Indigo | 5.13 | | | 7.40 | 0.038 | 5.49 |
| Acetylchloride | 3.86 | | | 11.85 | 0.046 | |
| acetic anhydride | | 5.90 | | 5.17 | 0.03 | |
| 2-Thiopheneacetyl chloride | 1.90 | | | 427.57 | 0.81 | |
| 2-(4-((2-ethylhexyl)oxy)phenyl)acetyl chloride | 4.20 | | | 220.50 | 0.92 | |
| NBS | 1.68 | | | 37.28 | 0.06 | |
| 1,4-Dioxane | | 4.30 | | 11.20 | 0.05 | |
| Xylene | | 5.00 | | 10.40 | 0.05 | |
| Dichloromethane | | | 500 | 2.14 | 1.07 | |
| Silica gel | | | 80 | 8.0 | 0.64 | |
| Chloroform | | | 500 | 3.56 | 1.78 | |

## *2. Characterization data of intermediates and target compounds*

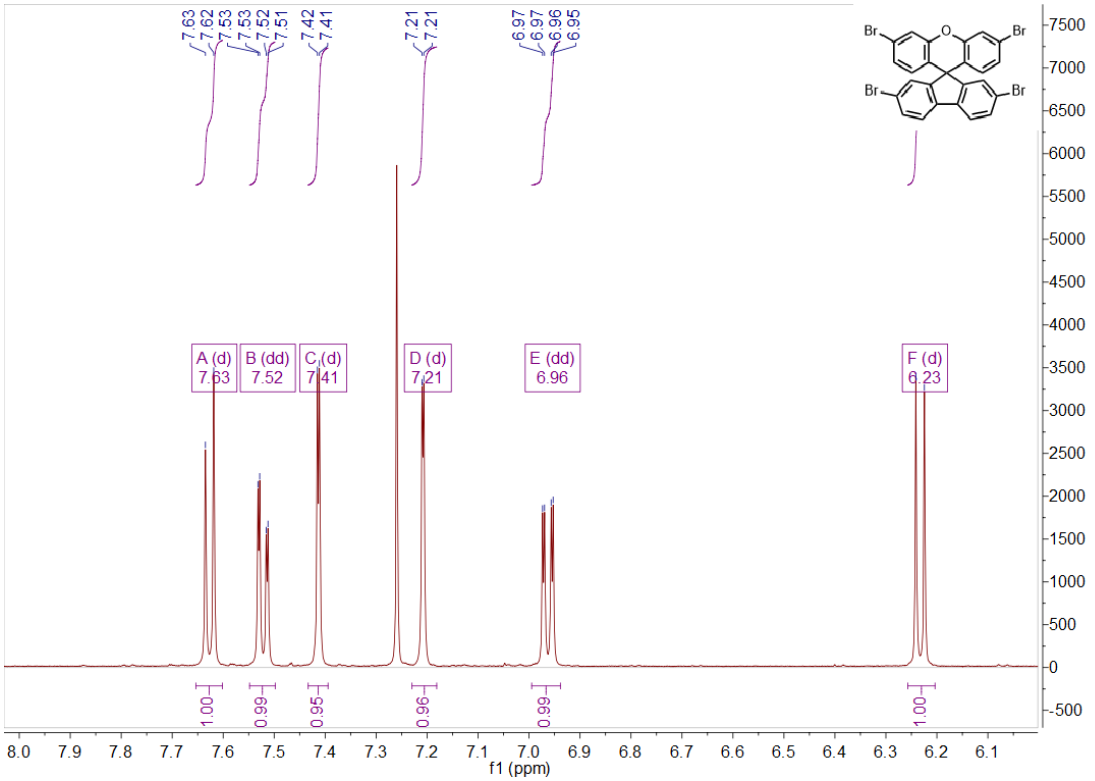


***Figure S1***. *$^1$H NMR spectra of 4Br-SFX ($CDCl_3$, 298K).*

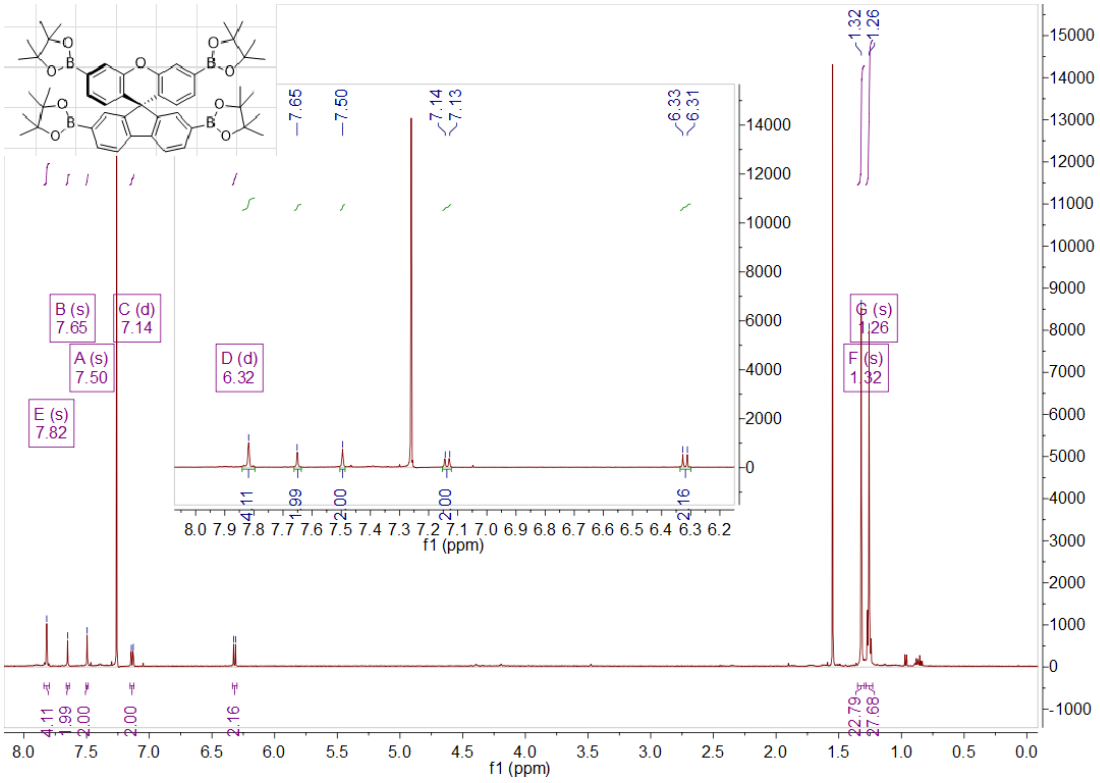


***Figure S2***. *$^1$H NMR spectra of 4Bpin-SFX ($CDCl_3$, 298K).*

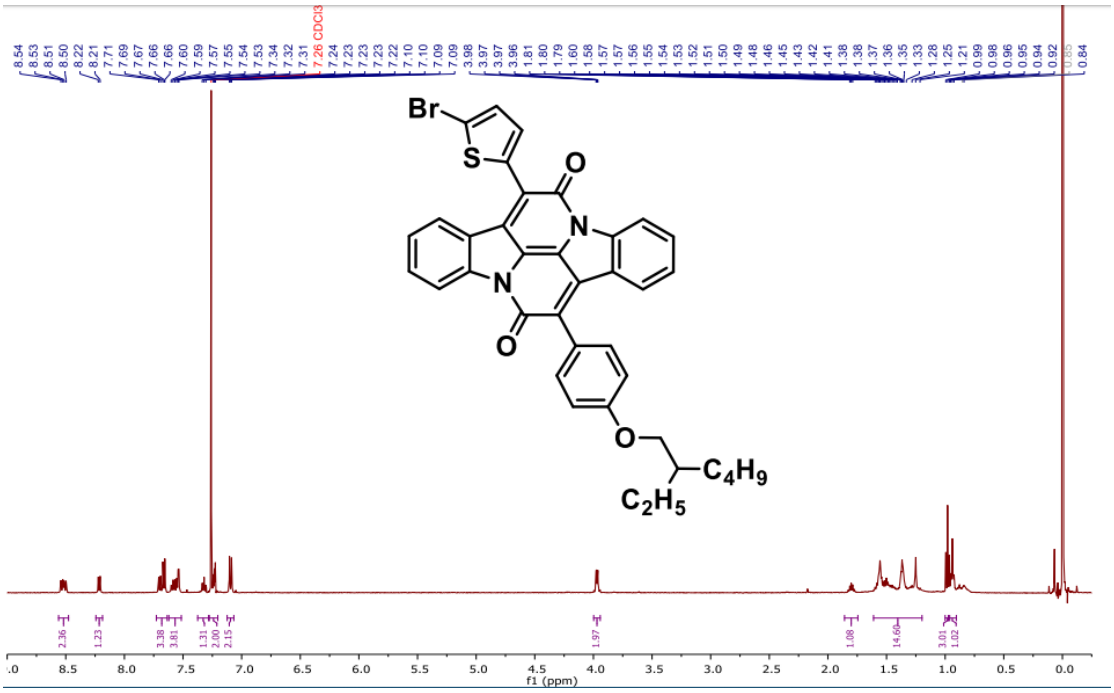


***Figure S3***. *$^1$H NMR spectra of bromo-BAI ($CDCl_3$, 298K).*

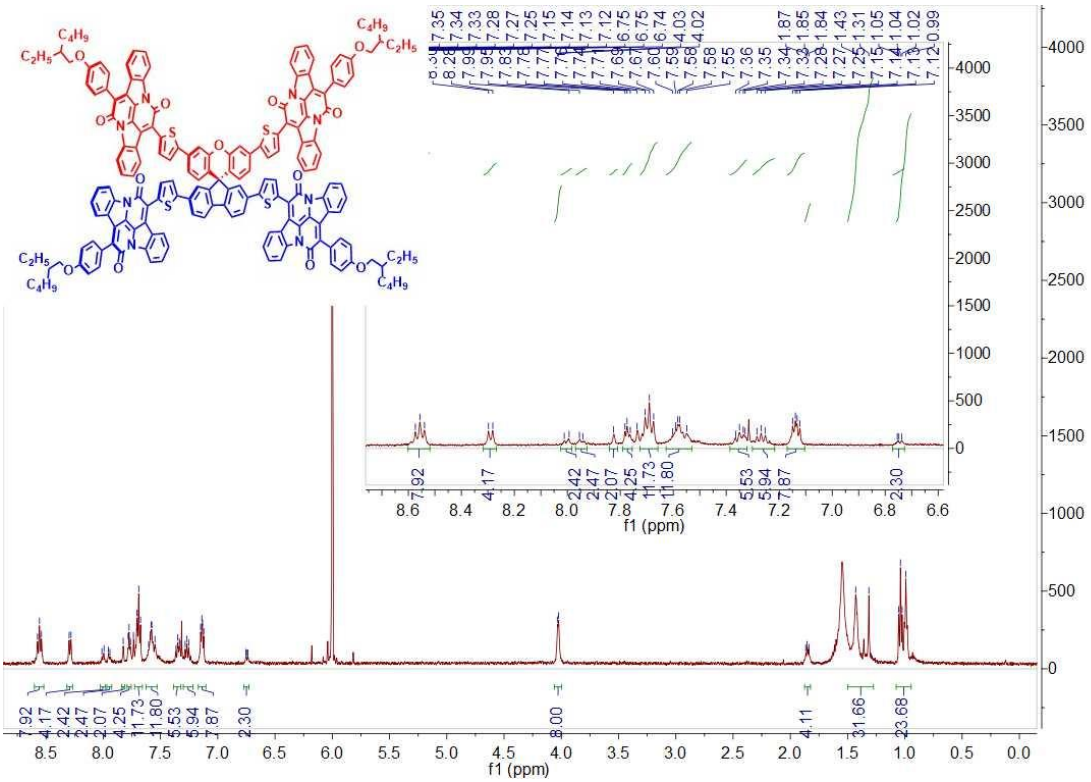


***Figure S4***. *$^1$H NMR spectra of **4BAI-SFX** ($C_2D_2Cl_4$, 358 K).*

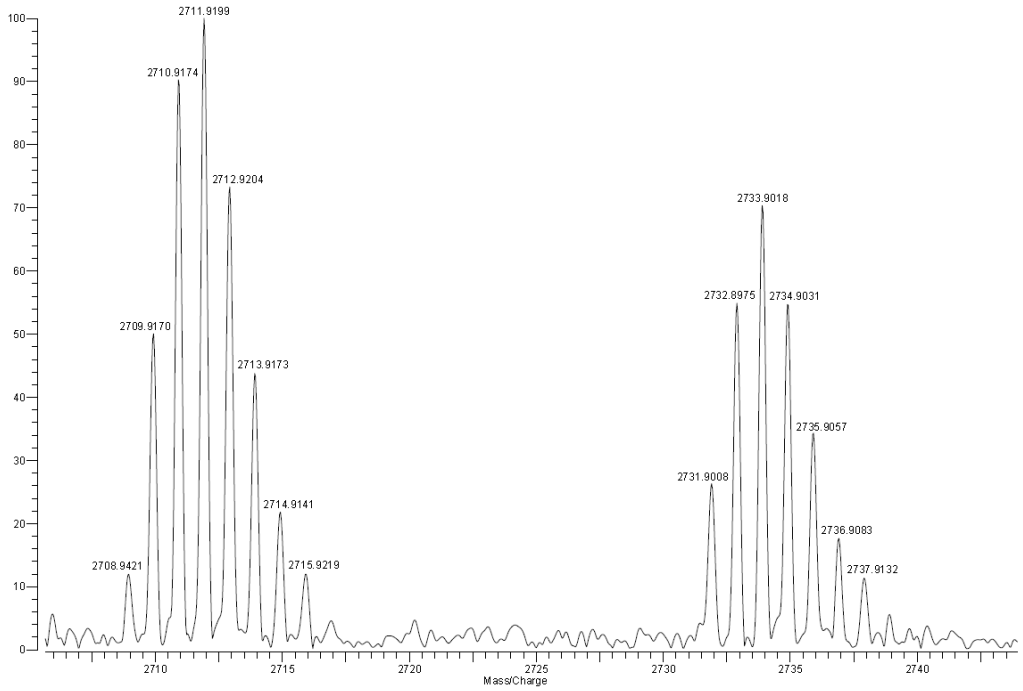


***Figure S5**. MALDI-TOF spectrum for 4BAI-SFX.*

## *3. Thermogravimetric analysis (TGA) curves*

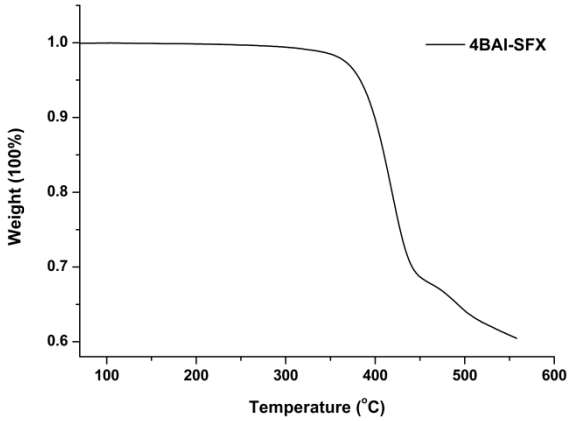


***Figure S6**. Thermogravimetric analysis (TGA) curves of 4BAI-SFX in a nitrogen atmosphere.*

## *4. Summary of UV-vis, CV, and DFT calculations*

***Table S3**. Summarized results of photophysics, electrochemistry, and DFT calculations.*

| Compd. | UV-Vis[a] | | | | Cyclic Voltammetry[b] | | | Calculated FMOs | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ /nm | $\varepsilon_{max}$ /$M^{-1}$ $cm^{-1}$ | $\lambda_{onset}$ /nm | $E_g^{opt}$ /eV | $E_{HOMO}$ /eV | $E_{LUMO}$ /eV | $E_g^{Elec}$ /eV | $E_{HOMO}$ /eV | $E_{LUMO}$ /eV | $E_g^{Calc}$ /eV |
| **4BAI-SFX** | 596 | 145300 | 687 | 1.80 | −5.34 | −3.59 | 1.75 | −4.93 | −2.84 | 2.09 |

[a] Measured in dilute chloroform solutions, [b] samples were prepared in degassed $CHCl_3$ solution with tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte at a scan rate of 100 mV $s^{-1}$.

## *References*


[1] M. Maciejczyk, A. Ivaturi, N. Robertson, SFX as a low-cost 'Spiro'hole-transport material for efficient perovskite solar cells, Journal of Materials Chemistry A, 4 (2016) 4855-4863.

[2] B. He, A.B. Pun, D. Zherebetskyy, Y. Liu, F. Liu, L.M. Klivansky, A.M. McGough, B.A. Zhang, K. Lo, T.P. Russell, New form of an old natural dye: bay-annulated indigo (BAI) as an excellent electron accepting unit for high performance organic semiconductors, Journal of the American Chemical Society, 136 (2014) 15093-15101.