

## Supporting Information

### Tailoring Pyrene Excimer Luminescence via Controlled Sulfur Oxidation

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## SI Experimental details

**SI-1 General information:** All the reagents and solvents used for the synthesis were purchased from Aldrich and Acros companies and used without further purification.  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, using tetramethylsilane (TMS) as the internal standard. The mass spectra were recorded using a Thermo Fisher ITQ1100 instrument. Elemental vario MICRO cube Elemental Analyzer was used to perform the elemental analysis.

**SI-2 Single crystal X-ray diffraction (SCXRD) data:** The crystals of Py-S, Py-SO, and Py-SOO were obtained through solvent diffusion method in a system of tetrahydrofuran and methanol. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) and control Software using the RAPID AUTO at room temperature. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the Olex2 programs. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were set as riding on the parent atoms after placing them in idealized positions around respective parent atoms. Drawings of molecular conformations and molecular stacking structures were made using Mercury software.

**SI-3 Photophysical measurements:** UV-vis spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Photoluminescence (PL) spectra and time-resolved PL spectra were carried out on a FLS980 Spectrofluorometer. Photoluminescence quantum yields (PLQYs) were measured using an integrating sphere apparatus on a FLS980 Spectrofluorometer.

**SI-4 Theoretical calculation:** All the density functional theory (DFT) calculations were carried out using Gaussian 09 (version D.01) package on a PowerLeader cluster.<sup>[1]</sup> The optimization of ground state and excited state geometries of single molecules was carried out at the level of M06-2X/6-31G(d, p). Time-dependent density functional theory (TD-DFT) was used for the calculation on vertical excitation energies at the level of M06-2X/6-31G(d, p).

**SI-5 Electrochemical characterization:** Cyclic voltammetry (CV) was performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk as the working electrode, a platinum wire as the auxiliary electrode with a porous ceramic wick, Ag/Ag $^+$  as the reference electrode, standardized for the redox couple ferricinium/ferrocene. The energy levels of the highest occupied

molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by the following equation:

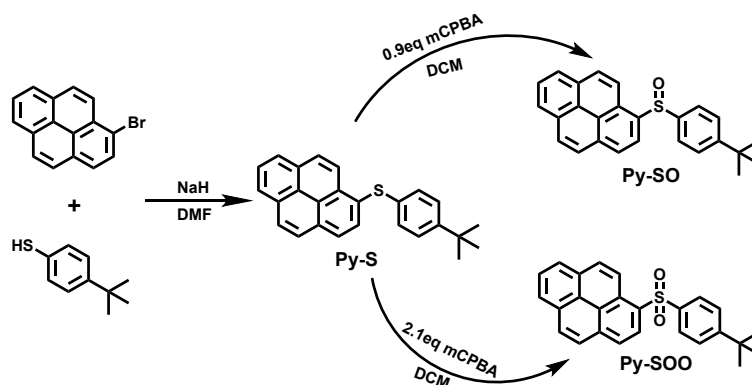
$$\text{HOMO (eV)} = - [E_{\text{ox}} - E(\text{Fc}/\text{Fc}^+) + 4.8]$$

$$\text{LUMO (eV)} = - [E_{\text{red}} - E(\text{Fc}/\text{Fc}^-) + 4.8]$$

**SI-6 Thermal stability measurements:** Thermal gravimetric analysis (TGA) was undertaken on a PerkinElmer thermal analysis system at a heating rate of 10 °C min<sup>-1</sup> and a nitrogen flow rate of 80 mL min<sup>-1</sup>. Differential scanning calorimetry (DSC) analysis was carried out using a NETZSCH (DSC-204) instrument at 10 °C min<sup>-1</sup> while flushing with nitrogen.

**SI-7 Device fabrication and performances:** ITO-coated glass was used as the substrate with a sheet resistance of 20 Ω square<sup>-1</sup>. The evaporation rate was controlled to be 0.03–0.1 nm s<sup>-1</sup> for organic layers, 0.01 nm·s<sup>-1</sup> for the LiF layer was and 0.3 nm·s<sup>-1</sup> for the Al layer. The PR650 spectra scan spectrometer was used to record EL spectrum and luminance-current density-voltage was measured by spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.

## SII Synthetic details



Scheme S1. Synthetic routes of Py-S, Py-SO, and Py-SOO.

### Synthesis of 4-(*tert*-butyl)phenyl(pyren-1-yl)sulfane (Py-S)

A mixture of 1-bromopyrene (2.82 g, 10 mmol) and 4-(*tert*-butyl)benzenethiol (2.00 g, 12 mmol) and N,N-Dimethylformamide (50 ml) was degassed and recharged with nitrogen under ice bath. Then sodium hydride (0.29 g, 12 mmol) was added in the mixture and the mixture was degassed and recharged with nitrogen again. After stirred 10 minutes under ice bath, the mixture was heated under reflux for 12 h. The cooled reaction mixture poured into ice water and extracted with dichloromethane. The organic phase was filtered and concentrated in a vacuum. It was purified via silica gel chromatography by petroleum ether and dichloromethane to afford white solid **Py-S** in 87 % yield (3.19 g). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ 8.72 (d, *J* = 9.1 Hz, 1H), 8.28 (d, *J* = 7.6 Hz, 2H), 8.22 – 8.16 (m, 3H), 8.15 – 8.07 (m, 3H), 7.34 – 7.30 (m, 2H), 7.26 – 7.19 (m, 2H), 1.31 (s, 9H). GC/MS, EI (mass *m/z*): 365.948 [M<sup>+</sup>]. Anal. calcd for C<sub>26</sub>H<sub>22</sub>S: C 85.20, H 6.05, S 8.75; found: C 85.59, H 6.27, S 9.16.

### Synthesis of 1-((4-(*tert*-butyl)phenyl)sulfinyl)pyrene (Py-SO)

**Py-S** (1.09 g, 3 mmol) dissolved in dichloromethane (30 ml) and *m*-chloroperoxybenzoic acid (0.47 g, 2.7 mmol) was slowly added into the mixture under ice bath. The mixture was stirred under ice bath for 30 minutes. The reaction was then stopped, removed the solvent under reduced pressure and the crude was purified via silica gel chromatography by dichloromethane and acetone to afford the pale-white powder **Py-SO** in 73 % yield (0.84 g). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ 8.65 (dd, *J* = 8.7, 6.8 Hz, 2H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.34 (dd, *J* = 7.7, 2.6 Hz, 2H), 8.26 (dd, *J* = 18.1, 9.1 Hz, 2H), 8.18 – 8.12 (m, 2H), 7.70 – 7.66 (m, 2H), 7.47 – 7.44 (m, 2H), 1.27 (s, 9H).

GC/MS, EI (mass m/z): 382.962 [M<sup>+</sup>]. Anal. calcd for C<sub>26</sub>H<sub>22</sub>SO: C 81.64, H 5.80, S 8.38, O 4.18; found: C 82.09, H 6.10, S 8.61.

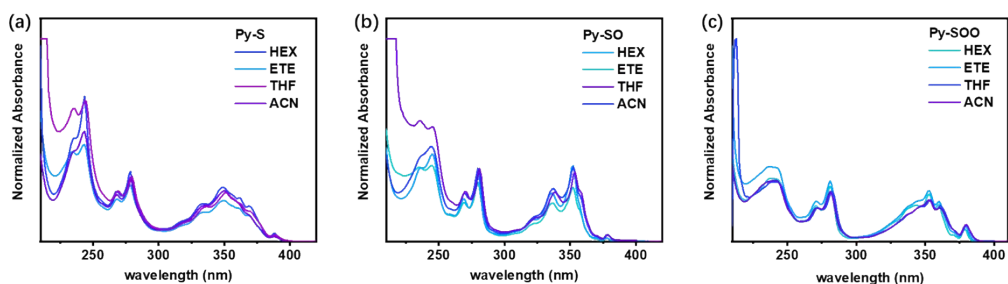
#### Synthesis of 1-((4-(tert-butyl)phenyl)sulfonyl)pyrene (Py-SOO)

**Py-S** (1.09 g, 3 mmol) dissolved in dichloromethane (30 ml) and *m*-chloroperoxybenzoic acid (1.08 g, 6.3 mmol) was slowly added into the mixture under ice bath. The mixture was stirred under ice bath for 30 minutes. The reaction was then stopped, removed the solvent under reduced pressure and the crude was purified via silica gel chromatography by dichloromethane and acetone to afford the pale-white powder **Py-SOO** in 87 % yield (1.04 g). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ 9.07 (d, *J* = 9.4 Hz, 1H), 8.94 (d, *J* = 8.2 Hz, 1H), 8.40 – 8.34 (m, 3H), 8.31 (dd, *J* = 11.3, 9.2 Hz, 2H), 8.21 – 8.13 (m, 2H), 8.01 – 7.95 (m, 2H), 7.57 – 7.51 (m, 2H), 1.28 (s, 9H). GC/MS, EI (mass m/z): 397.890 [M<sup>+</sup>]. Anal. calcd for C<sub>26</sub>H<sub>22</sub>SO<sub>2</sub>: C 78.36, H 5.56, S 8.04, O 8.03; found: C 78.39, H 5.78, S 8.03.

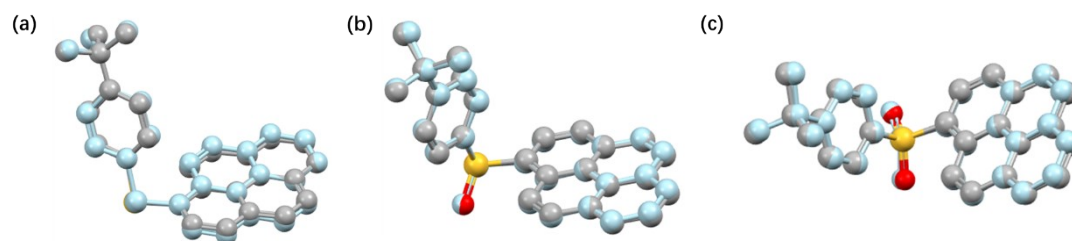
### SIII Figures and tables

Table S1. Crystallographic data of Py-S, Py-SO, and Py-SOO.

compound	Py-S	Py-SO	Py-SOO-A	Py-SOO-B
crystal color	light green	colorless	colorless	light green
empirical formula	C <sub>26</sub> H <sub>22</sub> S	C <sub>26</sub> H <sub>22</sub> SO	C <sub>26</sub> H <sub>22</sub> SO <sub>2</sub>	C <sub>26</sub> H <sub>22</sub> SO <sub>2</sub>
formula weight	366.49	383.50	398.49	398.49
<i>T</i> [K]	293.0	293.0	293.0	293.0
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
<i>a</i> [Å]	16.433(3)	13.255(8)	15.638(4)	11.7385(11)
<i>b</i> [Å]	10.6771(18)	13.562(6)	8.2711(16)	14.8718(15)
<i>c</i> [Å]	12.0421(18)	11.549(6)	17.359(4)	12.6273(13)
<i>α</i> [°]	90	90	90	90
<i>β</i> [°]	109.391(6)	104.150(18)	115.915(7)	110.919(4)
<i>γ</i> [°]	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1993.0(6)	2013.2(18)	2019.6(8)	2059.1(4)
<i>Z</i>	4	4	4	4
<b>F(000)</b>	776	812.0	840.0	840
density [g·cm <sup>-3</sup> ]	1.221	1.265	1.311	1.285
<i>μ</i> [mm <sup>-1</sup> ]	0.170	0.174	0.180	0.177
reflections collected	48453	37308	76717	49713
unique reflections	4558	4624	4642	4742
<i>R</i> (int)	0.0696	0.1433	0.0491	0.0413
<b>GOF</b>	1.027	1.027	1.065	1.044
<i>R</i> <sub>1</sub> [ <i>I</i> >2σ( <i>I</i> )]	0.0637	0.0643	0.0524	0.0640
<i>ωR</i> <sub>2</sub> [ <i>I</i> >2σ( <i>I</i> )]	0.1639	0.1618	0.1359	0.1743
<i>R</i> <sub>1</sub> (all data)	0.1306	0.1672	0.0748	0.0840
<i>ωR</i> <sub>2</sub> (all data)	0.2269	0.2377	0.1605	0.1942
CCDC	2345269	2345270	2345271	2345272



**Fig. S1.** Absorption spectra of (a) Py-S, (b) Py-SO, and (c) Py-SOO in different solvents. HEX is hexane, ETE is ethyl ether, THF is tetrahydrofuran, and CAN is acetonitrile.



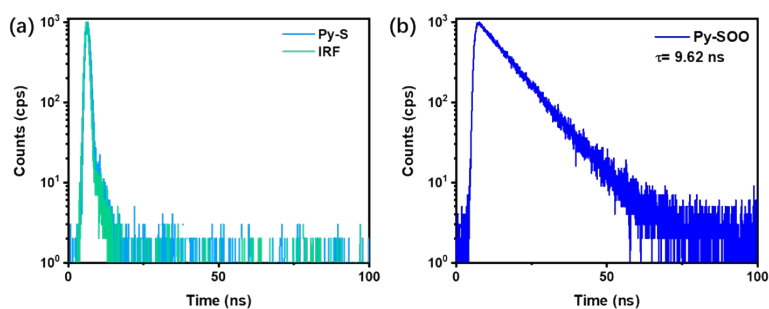
**Fig. S2.** Overlay diagram of (a) Py-S, (b) Py-SO, and (c) Py-SOO between their optimized ground state geometries and optimized excited state geometries.

**Table S2.** Bond length data of Py-S, Py-SO, and Py-SOO at their optimized ground state geometries and optimized excited state geometries.

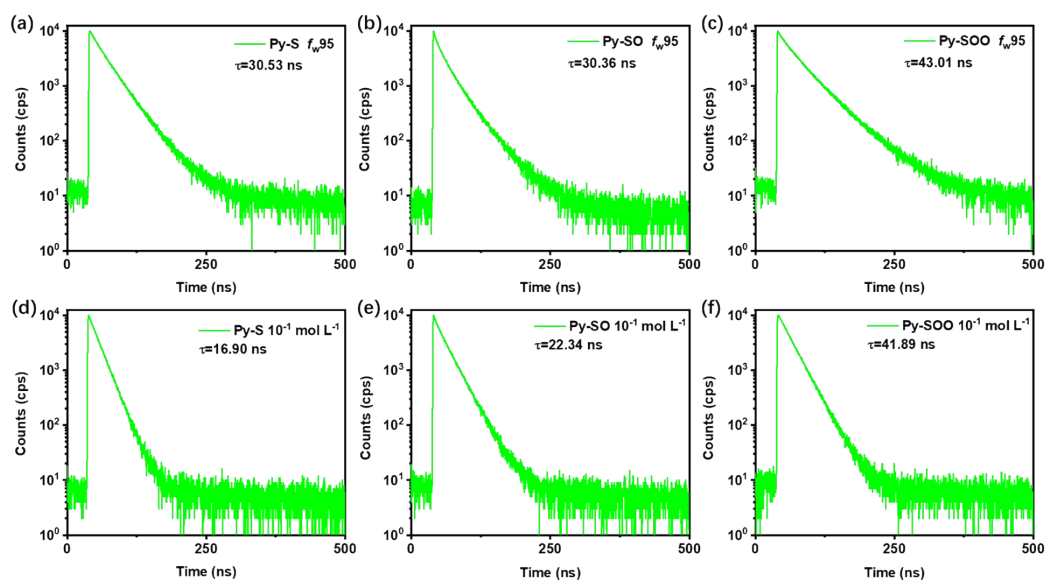
	optimized ground state geometries			optimized excited state geometries		
	Py(C-S) <sup>a</sup>	Ph(C-S) <sup>b</sup>	S=O	Py(C-S) <sup>a</sup>	Ph(C-S) <sup>b</sup>	S=O
<b>Py-S</b>	1.78245	1.78469		1.72516	1.78151	
<b>Py-SO</b>	1.80559	1.81045	1.50815	1.76167	1.81886	1.51287
<b>Py-SOO</b>	1.79366	1.78381	1.46083/1.46198	1.76820	1.77915	1.46442/1.46237

<sup>a</sup> Bond connecting pyrene and sulfur. <sup>b</sup> Bond connecting benzene and sulfur.

Compared to Py-SO, Py-SOO has shorter Py(C-S), Ph(C-S), and S=O bonds, indicating its structural rigidity.

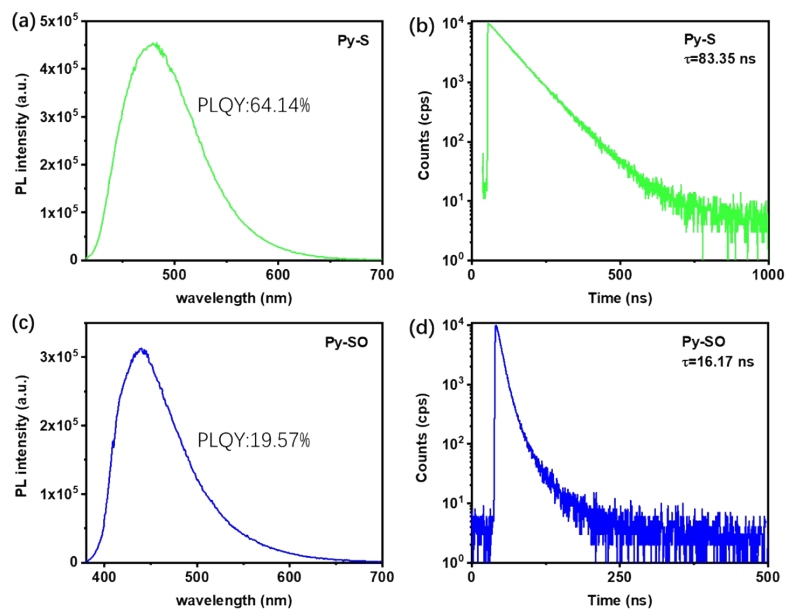


**Fig. S3.** Time-resolved PL spectra of (a) Py-S and (b) Py-SOO in THF solution with a concentration of  $10^{-5}$  mol L $^{-1}$ . The time-resolved PL spectrum of Py-S is superposed on instrument response function (IRF), indicating a very short lifetime of Py-S in its monomer state. Time-resolved PL spectrum of Py-SO cannot be recorded due to its very weak fluorescence.

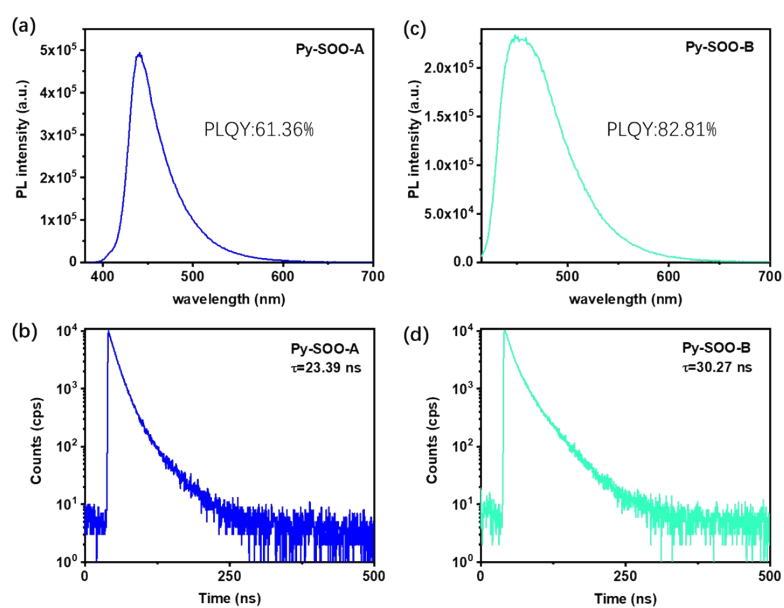


**Fig. S4.** Time-resolved PL spectra of (a) Py-S, (b) Py-SO, and (c) Py-SOO in THF solution with a concentration of  $10^{-1}$  mol L $^{-1}$ . Time-resolved PL spectra of (d) Py-S, (e) Py-SO, and (f) Py-SOO in THF:H $_2$ O mixture with a H $_2$ O fraction ( $f_w$ ) of 95%.



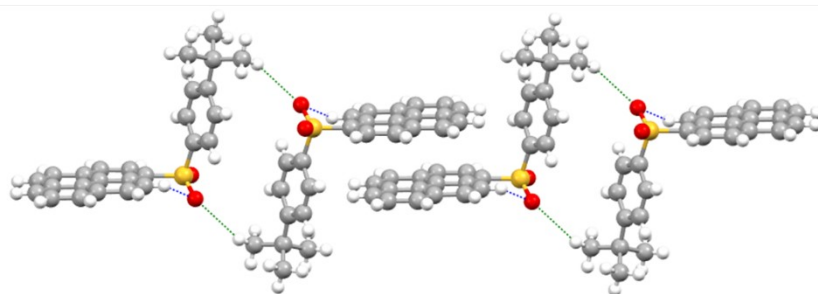


**Fig. S5.** PL spectra of (a) Py-S and (b) Py-SO crystals. Time-resolved PL spectra of (c) Py-S and (d) Py-SO crystals.

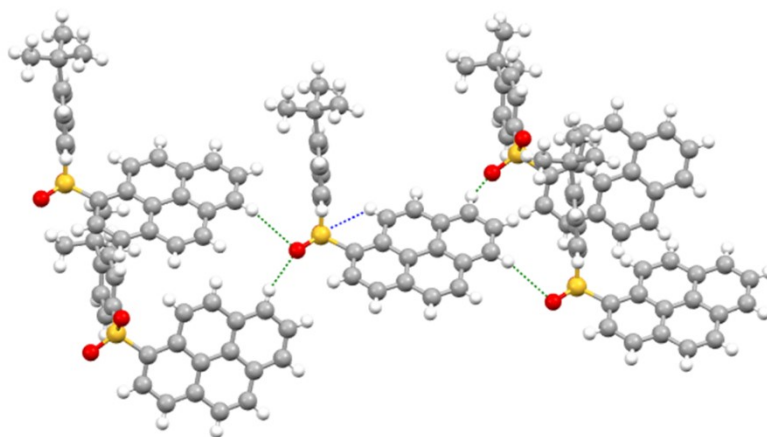


**Fig. S6.** PL spectra of (a) Py-SOO-A (b) Py-SOO-B crystals. Time-resolved PL spectra of (c) Py-SOO-A and (d) Py-SOO-B crystals.

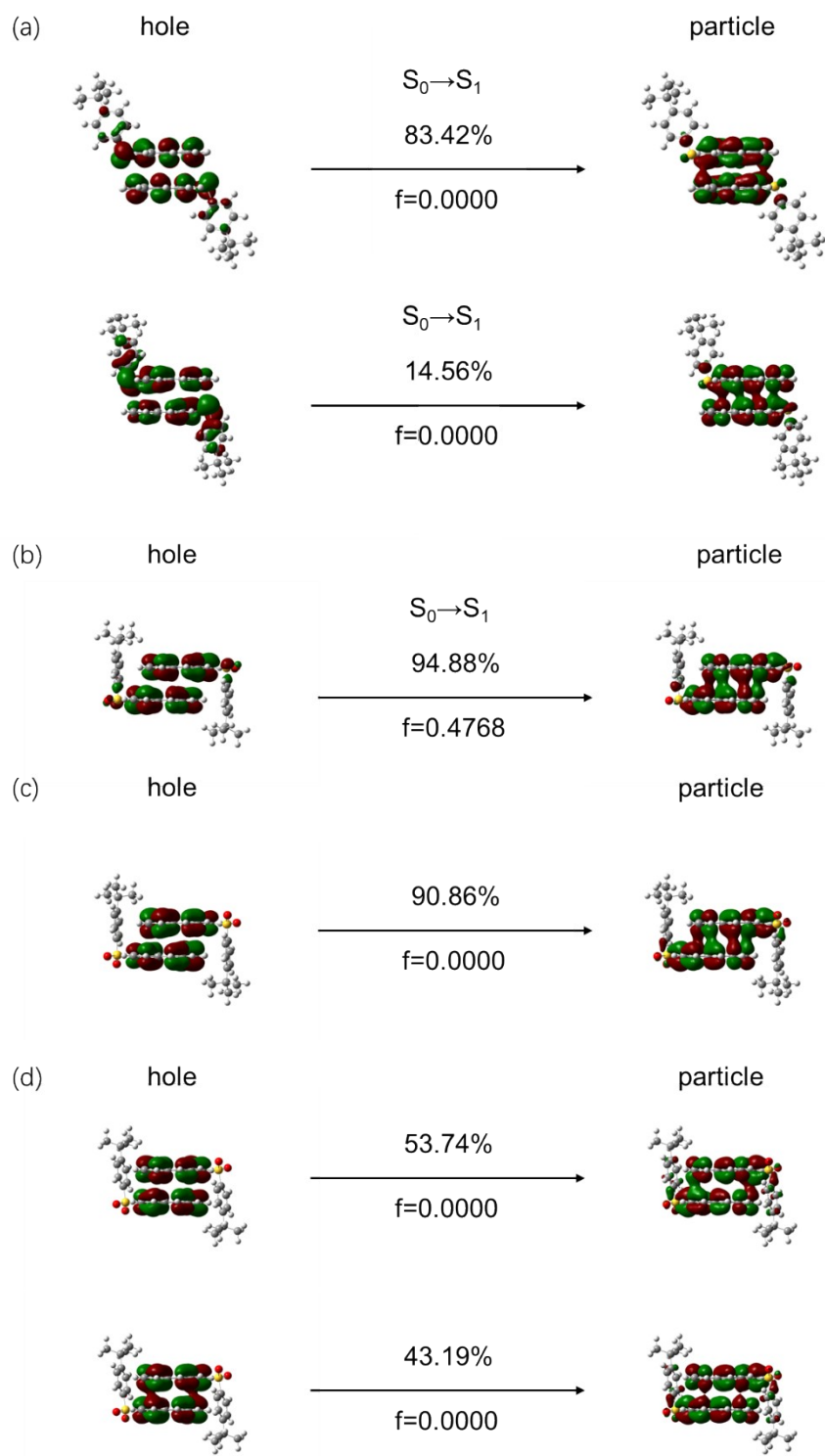
Py-SOO-A



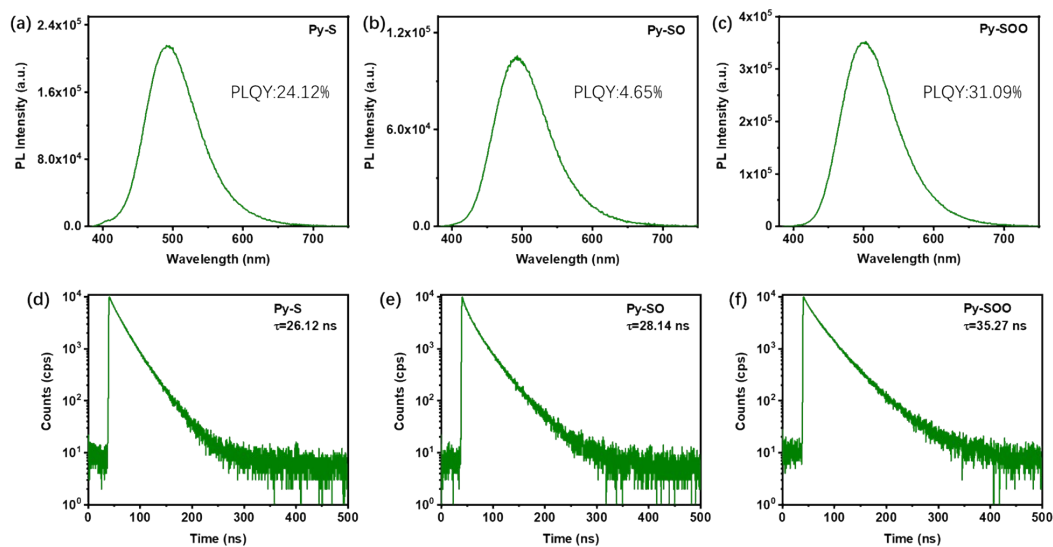
Py-SOO-B



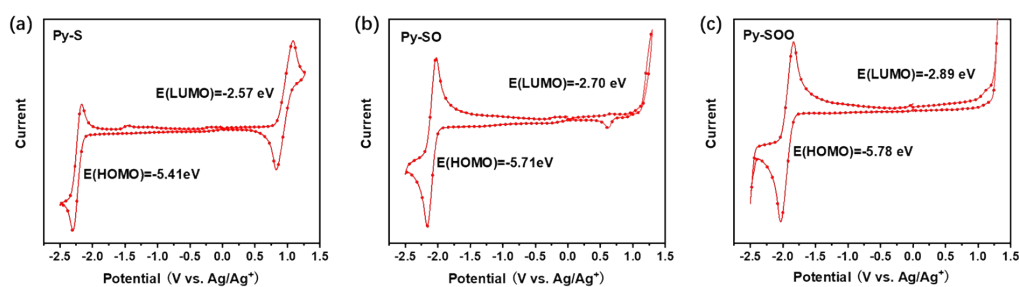
**Fig. S7.** Analysis of intermolecular hydrogen bonds in Py-SOO-A and Py-SOO-B crystals.



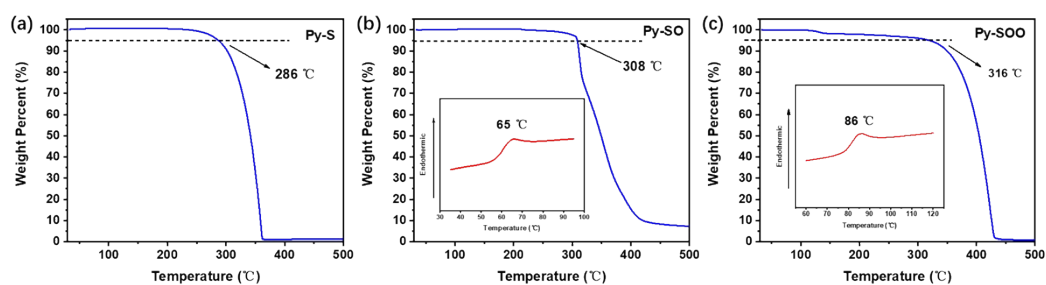
**Figure S8.** NTOs of (a) Py-S dimer, (b) Py-SO dimer, (c) Py-SOO-A dimer, and (d) Py-SOO-B dimer directly taken out from the crystal packing structures.



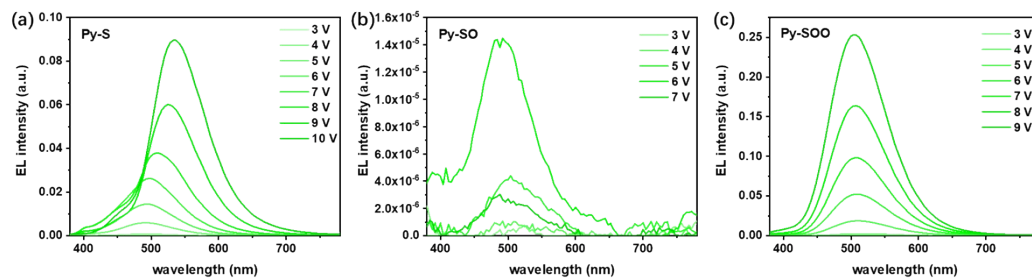
**Figure S9.** PL spectra and PLQY of (a) Py-S, (b) Py-SO, and (c) Py-SOO in their evaporated films. Time-resolved PL spectra of (d) Py-S, (e) Py-SO, and (f) Py-SOO in their evaporated films.



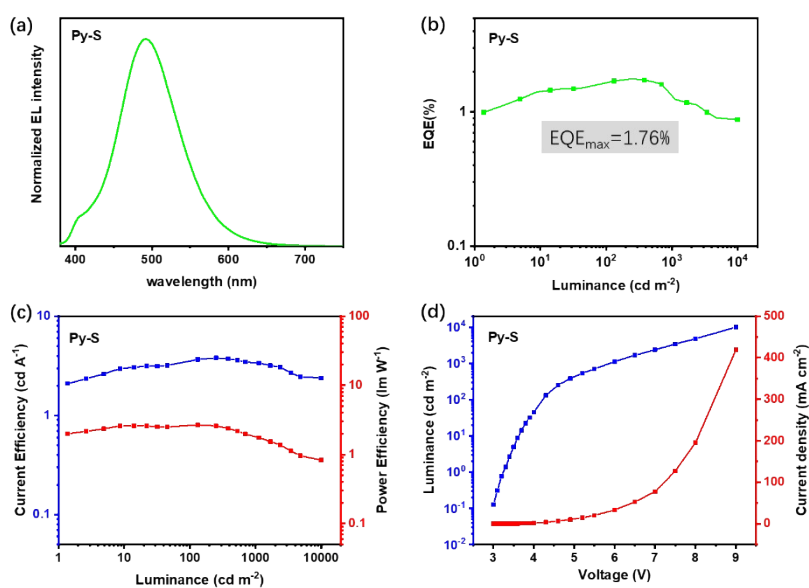
**Figure S10.** CV curves of (a) Py-S, (b) Py-SO, and (c) Py-SOO.



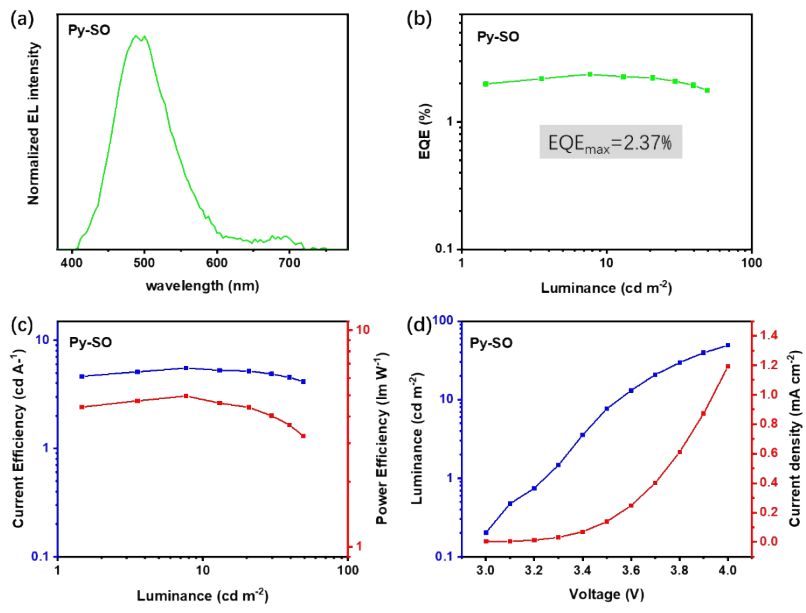
**Figure S11.** TGA and DSC curves of (a) Py-S, (b) Py-SO, and (c) Py-SOO. Py-S has no glass transition temperature.



**Figure S12.** EL spectra of (a) Py-S, (b) Py-SO, and (c) Py-SOO based devices under different voltages.



**Figure S13.** (a) EL spectra of Py-S recorded at 9 V. (b) EQE-luminance characteristic curves of Py-S. (c) Current efficiency-luminance-power efficiency curves of Py-S. (d) Luminance-voltage-current efficiency curves of Py-S.



**Figure S14.** (a) EL spectra of Py-SO. (b) EQE-luminance characteristic curves of Py-SO. (c) Current efficiency-luminance-power efficiency curves of Py-SO. (d) Luminance -voltage-current efficiency curves of Py-SO.

## SIV References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, **2013**.