Supporting Information

Supramolecular Steric Hindrance Effect on Morphologies and Photophysical Behaviors of Spirocyclic Aromatic Hydrocarbon Nanocrystals

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Experimental Section

All of chemicals were purchased from J&K Scientific Co. Ltd., and were used without further purification unless otherwise stated.

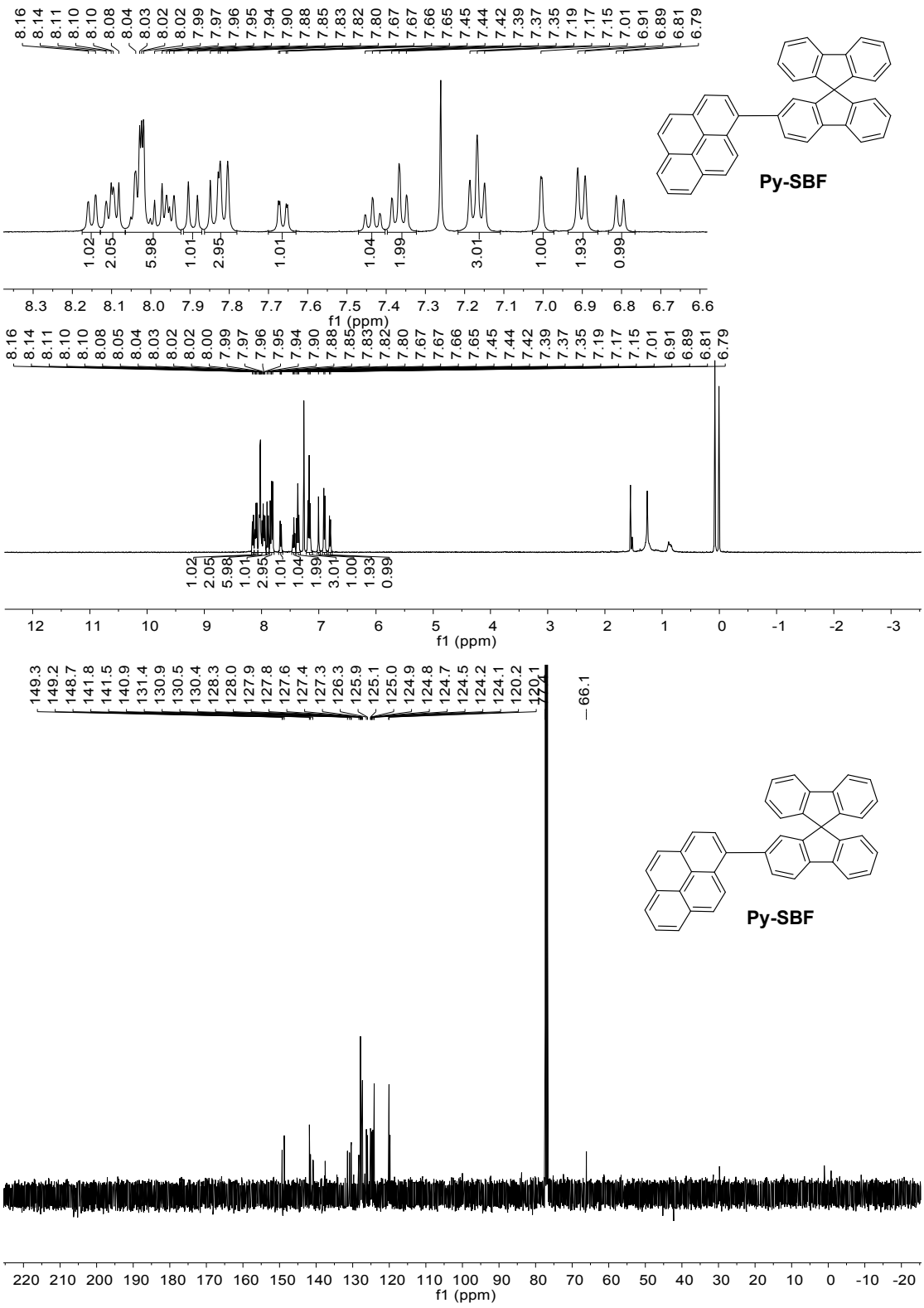
Preparation of micro/nano-crystals. The microcrystals of the three Py-SAHs were all prepared by reprecipitation method under the exact same conditions. Typically, 0.5 mg compounds in 1 mL THF solution was injected into a vigorously stirred water (5 mL), after being stirred for 5 min, the sample was left standing for about 48 h to stabilize the nanostructures. Subsequently, the samples underwent centrifugation and were washed with pure water three times.

Single crystal structure. Single crystals of the three molecules were grown by the solvent diffusion methods, typical growth conditions are presented in Table S1. Crystallographic information for the three compounds are summarized in Table S2 (these data can also be obtained free of charge from The Cambridge Crystallographic Data Centre: 1045049 (Py-SBF), 1045048 (Py-SFX), 1045049 (Py-SFDBX).

Characterization. For scanning electron microscopic (SEM) studies, a drop of 20 μL of samples was placed onto silicon substrates, and the solvent was left to evaporate. The samples were then examined with a field emission SEM (Hitachi S-4800) at an accelerating voltage of 5 kV. The transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) studies were performed in a JEM 2010F JEOL, operating at an accelerating voltage of 100 kV. The single crystal data collection was performed at around 100 or 298 K on a Bruker 2000 CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-2015 and refined against F^2 using SHELXL-2015. The power X-ray diffraction (XRD) patterns were performed on a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ = 1.54050 Å). The operating 2θ angle ranges from 5 to 30 Å, with the step length of 0.025°. Fluorescence lifetime and quantum efficiency were carried out with Edinburgh fluorescence spectrometer (FLS980) with an integrating sphere. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer.

ASE and microlaser characterization. The lasing spectra of the microcrystals were excited by a focused 325 nm laser through a confocal μ-PL system (OLYMPUS BX53). The size of light spot was about 20 μm in diameter. The luminescent light was collected through an optical multichannel analyzer (Princeton, Acton SP2500i) and the spectral resolution of the spectrometer is 0.167 nm. All measurements were performed at ambient atmosphere.

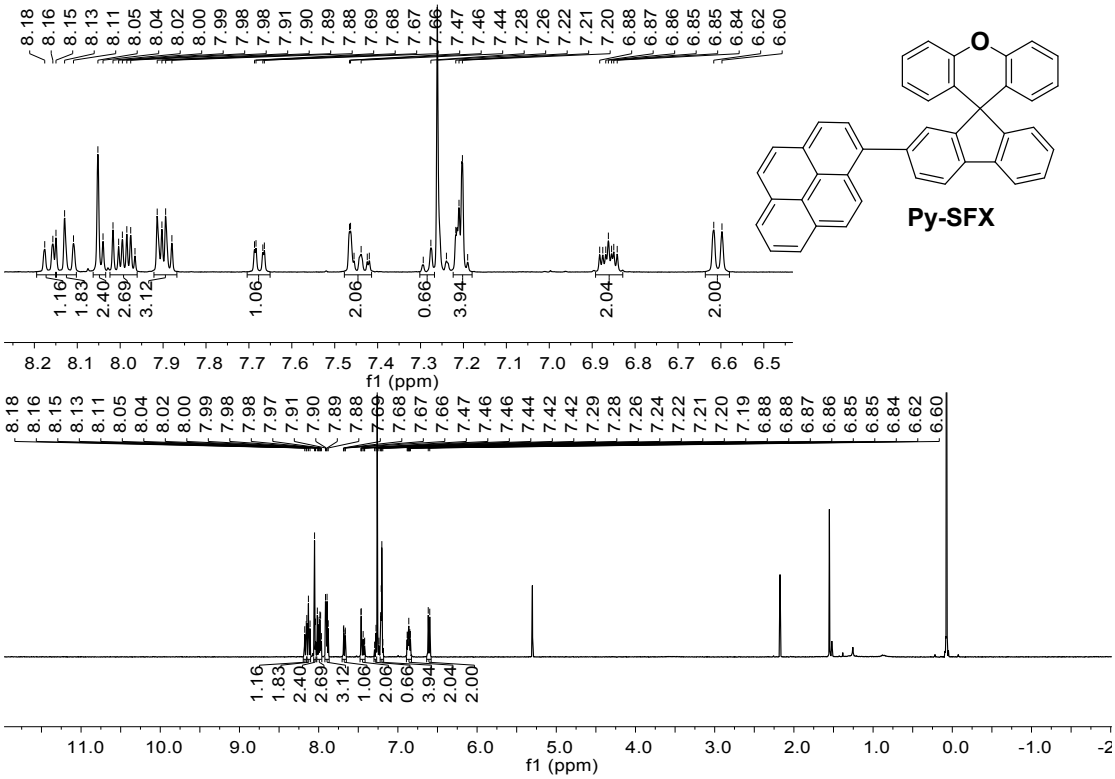
Synthesis of 1-(9,9'-spirobi[fluorene]-7-yl)pyrene (Py-SBF). In a three-necked schlenk flask (150 mL), BrSBF (1 g, 2.5 mmol.), 1-indole boric acid (1 g, 3 mol.), $Pd(PPh_3)_4$ (300 mg, 0.25 mol.) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which degassed toluene (30 mL) and K_2CO_3/KF aqueous solution (2 M, 5 mL, 10 eq) were injected into the flask through syringe. The ixture was heated up to 90 °C and stirred for 24 h. The mixture was extracted three times with CH_2Cl_2 and the organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether: CH_2Cl_2 = 6:1) to afford Py-SBF (0.8 g, 90%) as a pale white powder.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.14 (d, *J* = 7.3 Hz, 1H), 8.10 (dd, *J* = 7.5, 5.4 Hz, 2H), 8.06 – 7.92 (m, 6H), 7.90 – 7.88 (d, *J* = 9.3 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.67 – 7.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 – 7.42 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.35 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.15 (t, *J* = 7.5 Hz, 3H), 7.01 (s, 1H), 6.91 – 6.89 (d, *J* = 7.5 Hz, 2H), 6.81 – 6.79 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (400MHz, $CDCl_3$) δ 149.3, 149.2, 148.7, 141.8, 141.5, 140.9, 140.7, 137.5, 131.4, 130.9, 130.5, 130.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 127.3, 126.3, 125.9, 125.1, 125.0, 124.9, 124.7, 124.5, 124.2,

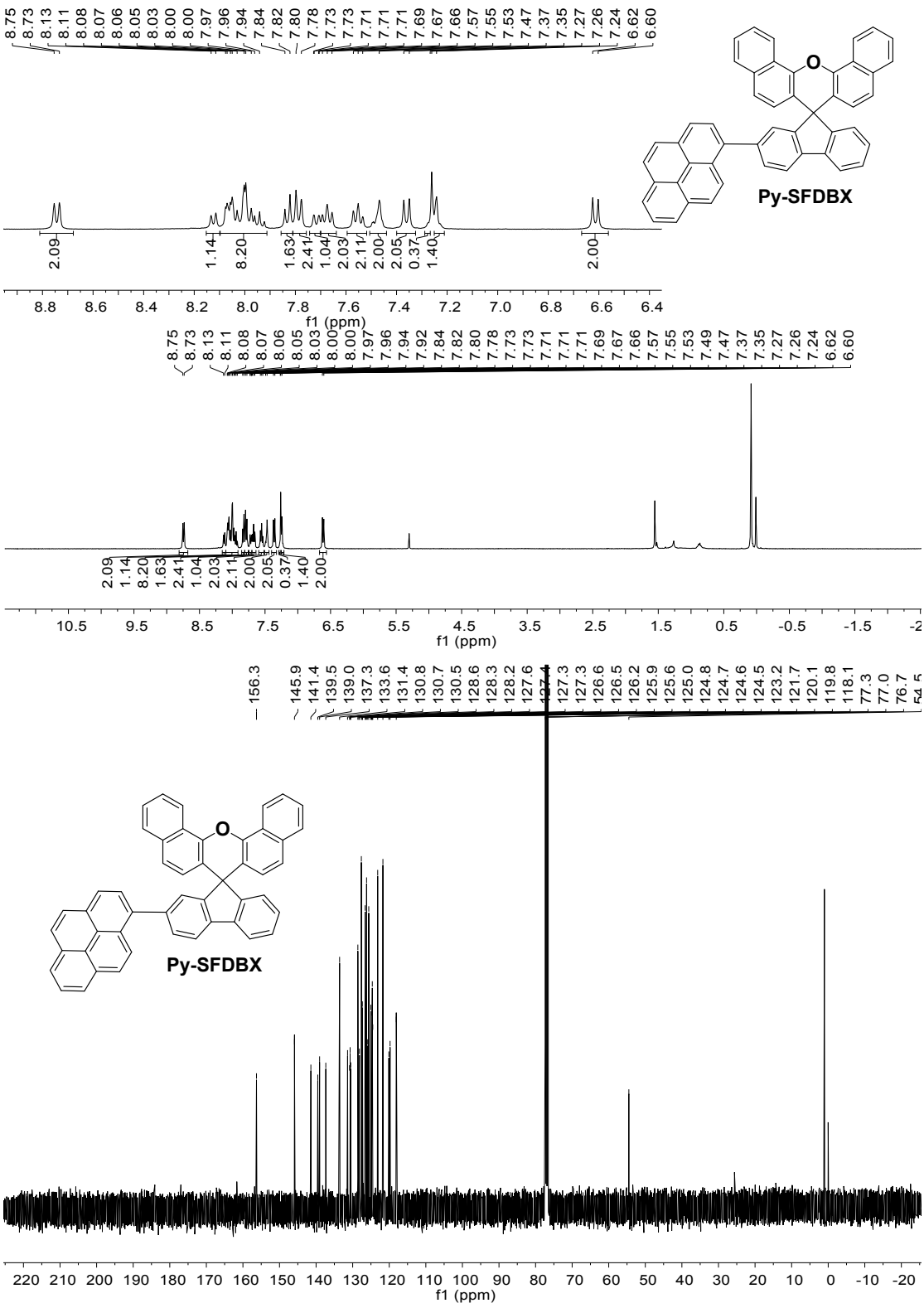
124.1, 120.2, 120.1, 66.1.

Synthesis of 2-(pyren-1-yl)spiro[fluorene-9,9'-xanthene] (Py-SFX). In a three-necked schlenk flask (150 mL), BrSFX (1 g, 2.5 mmol.), 1-indole boric acid (1 g, 3mmol.), $Pd(PPh_3)_4$ (300 mg, 0.25 mol.) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which degassed toluene (30 mL) and K_2CO_3/KF aqueous solution (2 M, 5 mL, 10 eq) were injected into the flask through syringe. Themixture was heated up to 90 °C and stirred for 24 h. The mixture was extracted three times with CH_2Cl_2 and the organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether : CH_2Cl_2 = 6:1) to afford Py-SFX (0.5 g, 60%) as a pale white powder.



^{1}H NMR (400MHz, $CDCl_3$, ppm) : δ 8.18 – 8.16 (d, *J* = 7.6 Hz, 1H), 8.15 – 8.11 (t, *J* = 8.2 Hz, 2H), 8.05 – 8.04 (m, 2H), 8.02 – 7.97 (m, 3H), 7.91 – 7.88 (m, 3H), 7.69 – 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.19 (m, 4H), 6.88 – 6.84 (m, 2H), 6.62 – 6.60 (d, *J* = 7.7 Hz, 2H).

Synthesis* of *2'-(pyren-1-yl)spiro[dibenzo[c,h]xanthene-7,9'-fluorene] (Py-SFDBX). In a three-necked schlenk flask (150 mL), BrSFDBX (3 g, 5.87 mmol.), 1-indole boric acid (1.7 g, 7.04mmol.), $Pd(PPh_3)_4$ (400mg, 0.35mmol.) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which toluene (15ml)/THF(15ml) and K_2CO_3/KF aqueous solution (2 M, 30mL) were injected into the flask through syringe. The mixture was heated up to 90^{o}C and stirred for 24 h. The mixture was extracted three times with CH_2Cl_2 and the organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether: CH_2Cl_2 = 4:1) to afford Py-BrSFDBX (1.9 g, 51%) as a pale white powder.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.73 (d, *J* = 8.3 Hz, 2H), 8.13 – 8.11 (d, *J* = 7.4 Hz, 2H), 8.08 – 7.92 (m, 8H), 7.84 – 7.82 (d, *J* = 8.0 Hz, 2H), 7.80 - 7.78 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.71 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.66 (t, *J* = 7.5 Hz, 2H), 7.57 – 7.53 (t, *J* = 7.3 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.37 – 7.35 (d, *J* = 8.6 Hz, 2H), 7.27 - 7.24 (m, 2H), 6.62 – 6.60 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 145.9, 141.4, 139.5, 139.0, 137.3, 133.6, 131.4, 130.8, 130.7, 130.5, 128.6, 128.3, 128.2, 127.6, 127.4, 127.3, 126.6, 126.5, 126.2, 125.9, 125.6, 125.0, 124.9, 124.8, 124.7, 124.6, 124.5,

123.2, 121.7, 120.1, 119.8, 118.1, 54.5.

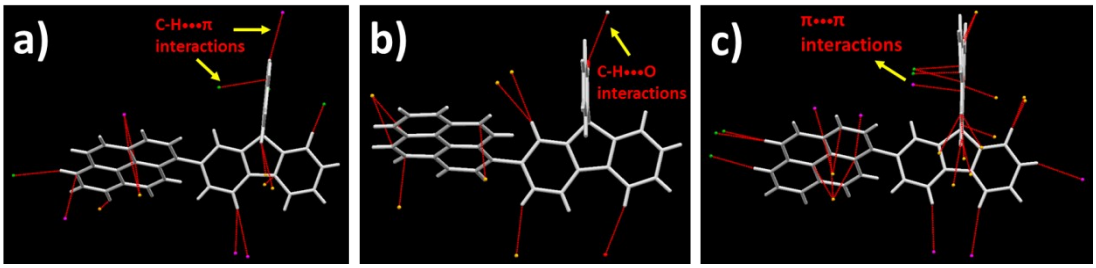


Figure S1. Intermolecular interactions of the three Py-SAHs in single crystal structures. (a) Py-SBF, (b) Py-SFX, (c) Py-SFDBX.

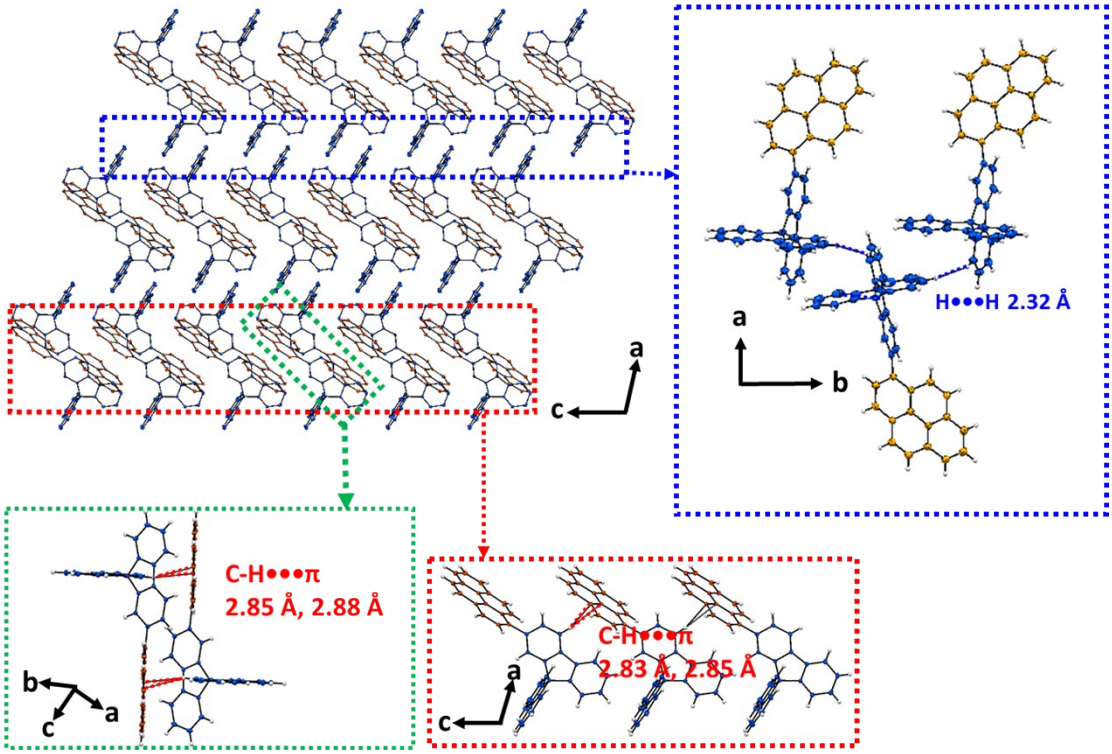


Figure S2. Molecular packing motifs of Py-SBF. The hydrogen atoms were omitted for clarity in packing.

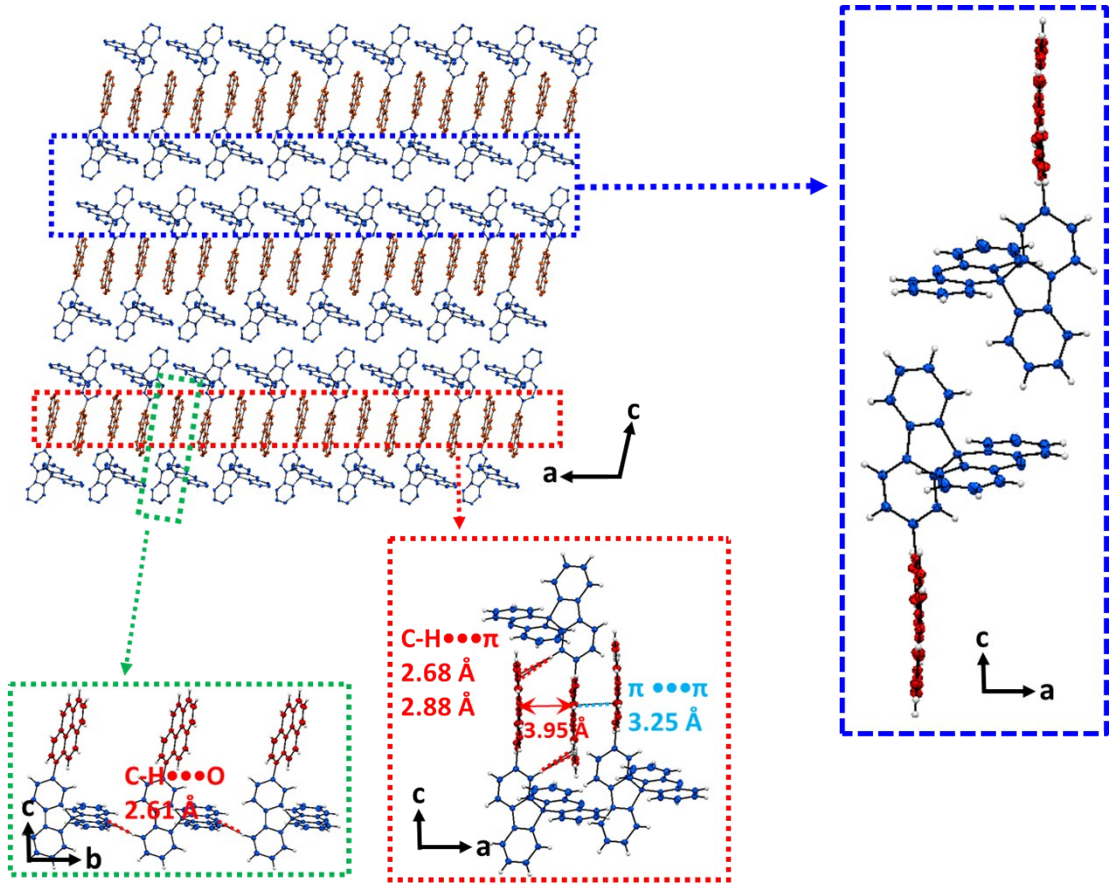


Figure S3. Molecular packing motifs of Py-SFX. The hydrogen atoms were omitted for clarity in packing.

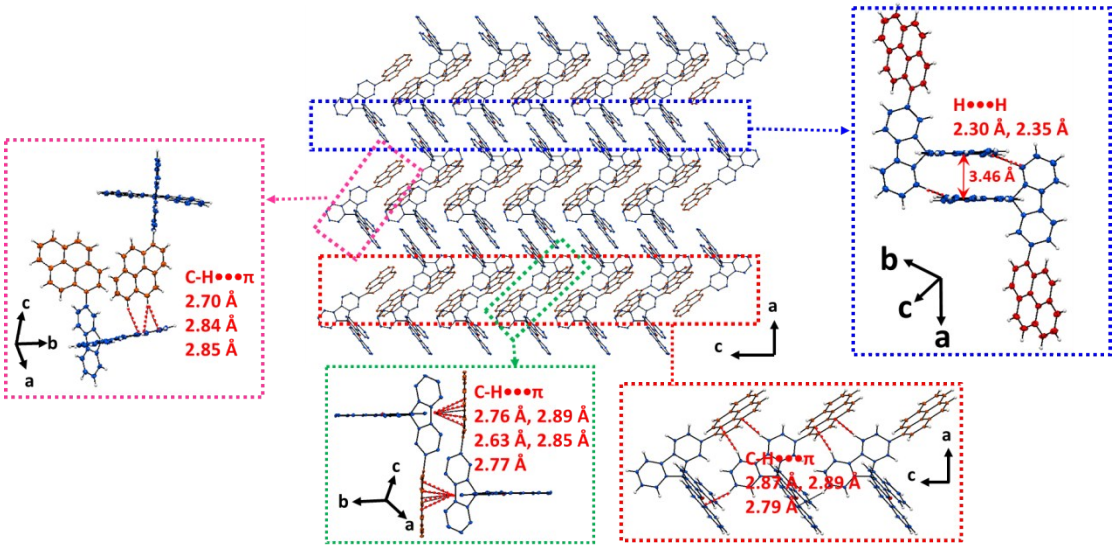


Figure S4. Molecular packing motifs of Py-SFDBX. The hydrogen atoms were omitted for clarity in packing.

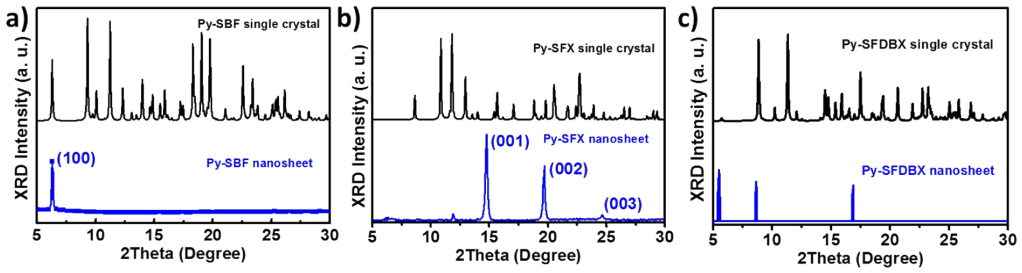


Figure S5. XRD patterns of the as-prepared Py-SAHs organic nanosheets (bottom) and the standard powder spectrum based on the single crystal data by using the DIAMOND software (top).

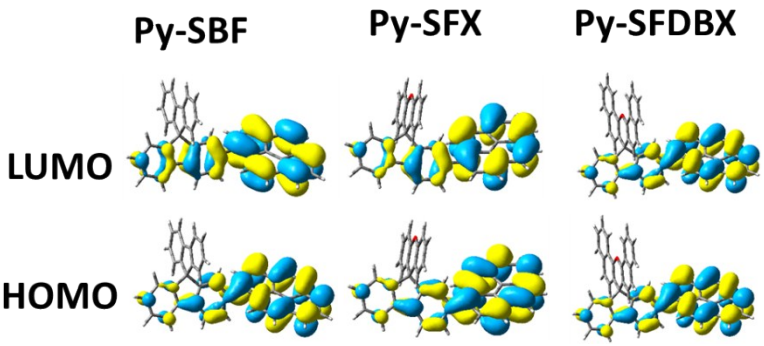


Figure S6. The frontier orbital distributions and corresponding energy levels of the Py-SAHs.

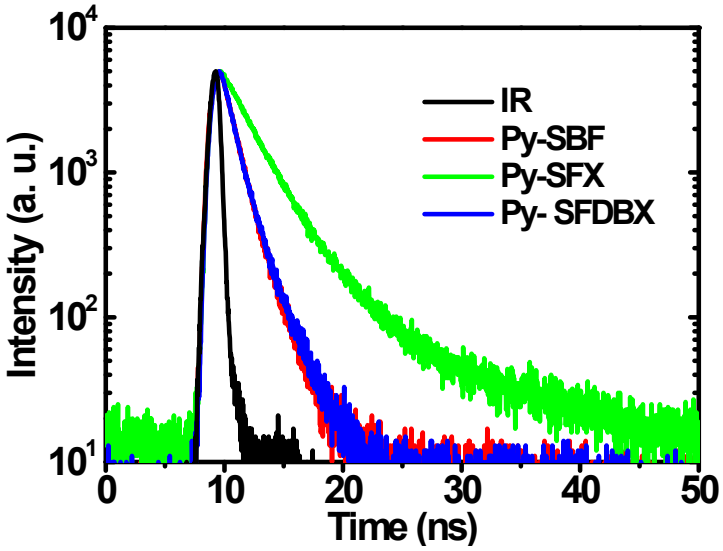


Figure S7. Time-resolved fluorescence of the three Py-SAHs micro-crystals by time-correlated single-photon counting measurement.

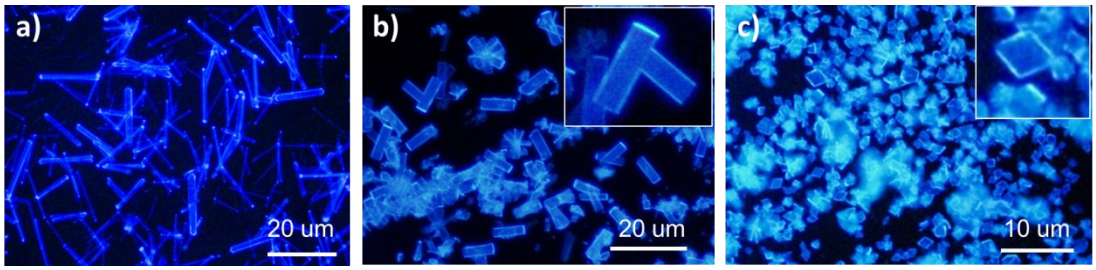


Figure S8. Fluorescence microscope images of a) Py-SBF wires; b) Py-SFX rectangular microplates and c) Py-SFDBX rhombic microsheets excited with UV band using mercury lamp as source.

Table S1. Solvent diffusion growth conditions of the different Py-SAHs compounds.

compound	Good solvent	Poor solvent	Growth time	Growth temperature
Py-SBF	tetrahydrofuran	isopropanol	14	25 °C
Py-SFX	tetrahydrofuran	isopropanol	30	25 °C
Py-SFDBX	tetrahydrofuran	isopropanol	7	25 °C

Table S2. Crystal data for the three Py-SAHs compounds.

Parameter	Py-SBF	Py-SFX	Py-SFDBX
Formula	$C_{41}H_{24}$	$C_{41}H_{24}O$	$C_{49}H_{28}O$
CCDC No.	1045049	1045048	1045050
fw [g/mol]	516.63	532.63	632.75
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P\,2_1/c$	P-1	$P\,2_1/c$
Color of crystal	white	white	yellow
a [Å]	14.999(5)	8.821(10)	15.5472(13)
b [Å]	11.913(4)	9.062(10)	12.2242(10)
c [Å]	16.835(5)	20.85(2)	17.3652(15)
α [°]	90	86.212(16)	90
β [°]	110.752(5)	79.334(15)	94.315(4)
γ [°]	90	64.024(15)	90
Z	4	2	4
Volume [$Å^3$]	2812.97	1472.19	3290.94
Density	1.220	1.202	1.277

Table S3. Optical/electrical properties of the three Py-SAHs.

Entry	$\lambda_{abs,\,max}$[a] (nm)	$\lambda_{PL,\,max}$ (nm)[b]			Φ[c] (%)	τ[d] (ns)	K_r/K_{nr}[e] (ns^{-1})	HOMO /eV	LUMO /eV
		Soln.	Film	Crystal					

Py-SBF	351/354/353	419/404,422	468/426	422	58/70	1.18	0.59/0.25	-5.51	-2.41
Py-SFX	350/355/350	420/406,426	469/428	431	60/67	2.34	0.29/0.14	-5.68	-2.39
Py-SFDBX	350/354/354	419/420	464/448	448	54/72	1.17	0.62/0.24	-5.70	-2.40

[a]The maximum absorption peaks of tetrahydrofuran solution/spin-coating film/microcrystal film.
[b]The maximum emission peak of tetrahydrofuran solution/spin-coating film/microcrystal film.
[c]Absolute fluorescent quantum efficiency of film/microrystal.
[d]The lifetime of microcrystal.
[e]The radiative/non-radiative rate constants of the microcrystals.