Supporting Information

Variable Segment Roles: Modulation of the Packing Modes, Nanocrystal Morphologies and the Optical Emissions

Sha-Sha Wang,[a†] Rong Rong,[a†] Ling-Zhi Jin,[a] Shan-Shan Yang,[a] Yin-Xiang Li,[a] He Zhang,[a] Yu-Wei Xiong,[c] Li-Tao Sun,[c] Hong-Tao Cao,[a] Ling-Hai Xie,*[a] Wei Huang,*[ab]

[a] Centre for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM),
Nanjing University of Posts & Telecommunications (NUPT)
9 Wenyuan Road, Nanjing 210023 (P.R. China) E-mail: iamlhxie@njupt.edu.cn

[b] Shaanxi Institute of Flexible Electronics (SIFE)
Northwestern Polytechnical University (NPU)
127 West Youyi Road, Xi'an 710072 (P.R. China) E-mail: wei-huang@njtech.edu.cn

[c] SEU-FEI Nano-Pico Center and Key Lab of MEMS of Ministry of Education
School of Electronic Science and Engineering
Southeast University
2 Sipailou, Nanjing 210096 (P. R. China)

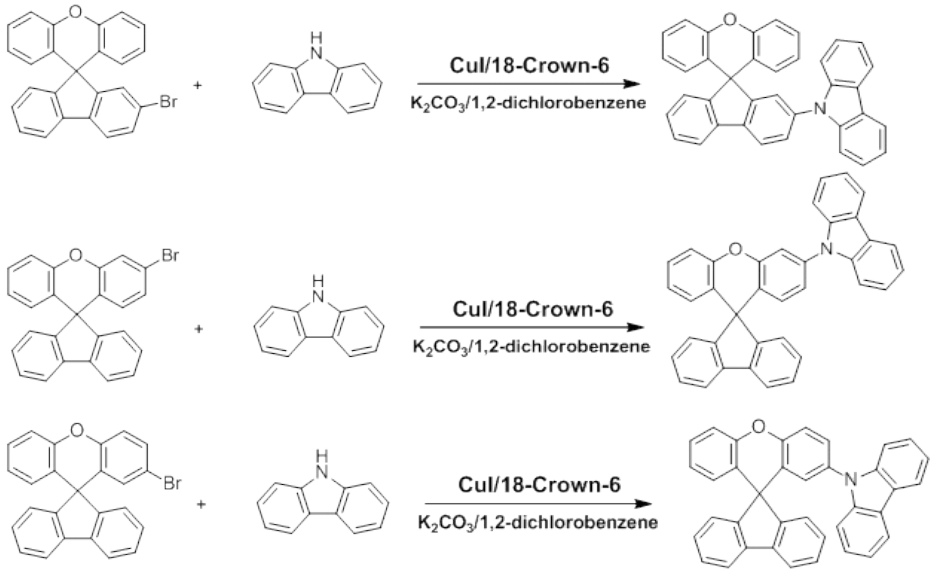
Experimental Section

Materials. The isomeric molecules of SFX-2-Cz, SFX-3'-Cz and SFX-2'-Cz were synthesized by condensation of bromospiro[fluorene-9,9'-xanthene] with carbazole in high yields and corresponding detailed synthesis processes are shown in Figure S1. 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 and single crystal structures. The microcrystals were fabricated through a classical reprecipitation method. Typically, the target compounds (0.1 mg) dissolved in THF (1 mL) was injected into a 5 mL of highly purified deionized water with Pluronic 123 (P123) (2 mg/mL) under vigorous stirring for 5 min, following aging at room temperature for 24 h to stabilize the nanostructures. Then, the nanocrystals with distinct morphologies can be formed in the mixed solution. At last, the nanocrystals underwent centrifugation and were washed with pure water at least four times. Furthermore, in order to further explore their nanocrystalline morphologies, a variety kinds of external conditions were used in Table S3. Single crystals of the three molecules were obtained by the solvent diffusion methods, the growth conditions are showed in Table S4. Crystallographic information files (CIFs) for the three compounds are summarized in Table S1 (these data can also be obtained free of charge from the Cambridge Crystallographic Data Centre; 1577085 (SFX-2-Cz), 1577086 (SFX-3'-Cz) and 1577084 (SFX-2'-Cz)).

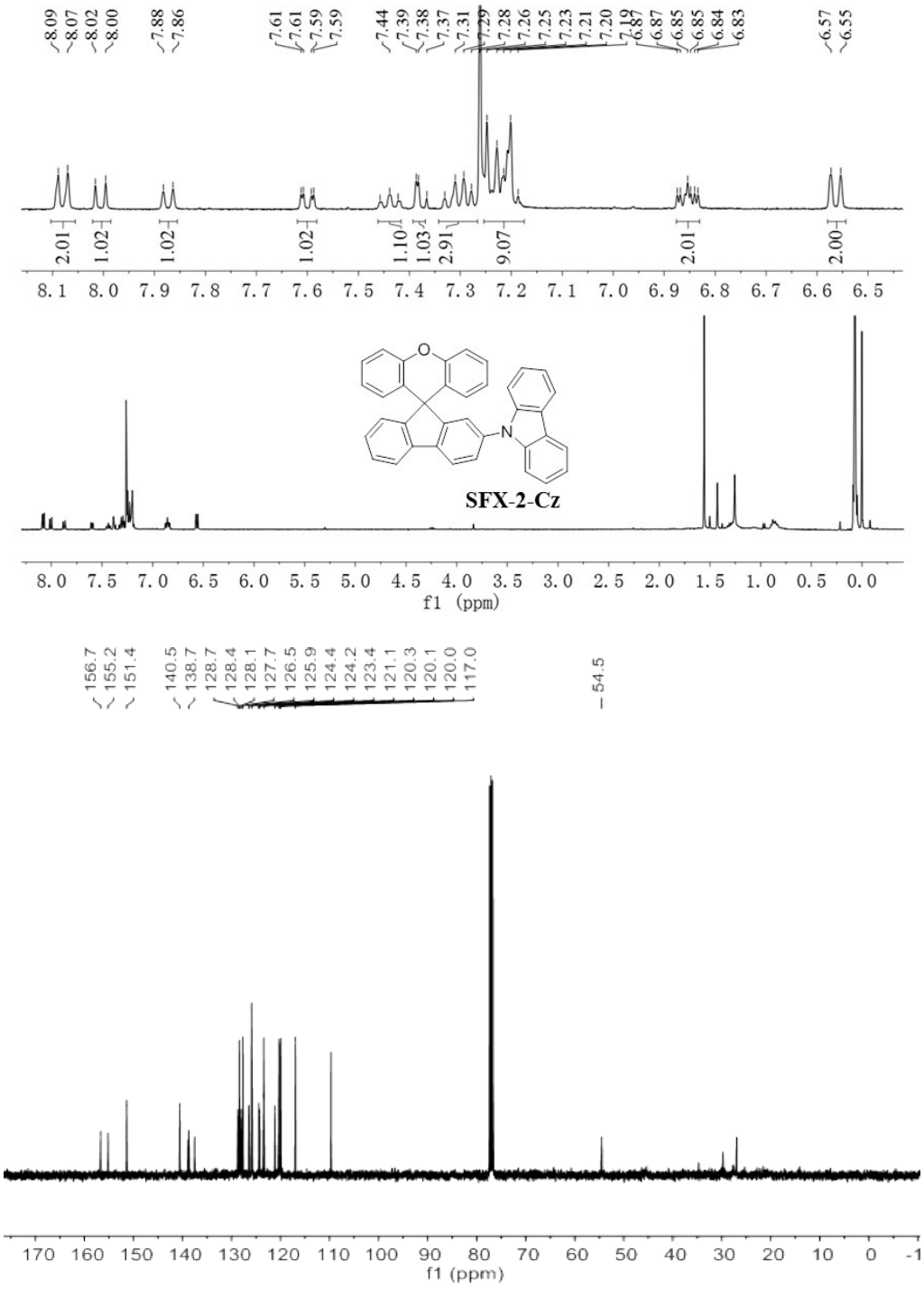
Characterization. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. For scanning electron microscopic (SEM) test, a drop of 10 μL target nanocrystals was deposited on the silicon substrates with the solvent evaporating completely, and 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 and operated under an accelerating voltage of 120kV, a drop of 20 μL colloidal dispersion was placed onto a carbon-coated copper grid. 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. X-ray diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer with Cu KR radiation (λ = 1.54050 Å). The operating 2θ angle ranges from 5 to 30 Å, with the step length of 0.025 Å. All the IE calculations were performed by density functional theory (DFT) at the Gaussian09 WB97XD/6-31+G(D) level based on their crystallographic data. Photoluminescence (PL) emission spectra was measured using a PerkinElmer LS55 spectrophotometer. Lifetimes were measured using an Edinburgh FLSP920 lifetime spectrometer with a 315 nm laser (typical pulse width: 55 ps; pulse repetition frequencies: 20 MHz).

Synthesis of SFX-2-Cz, SFX-3'-Cz and SFX-2'-Cz.

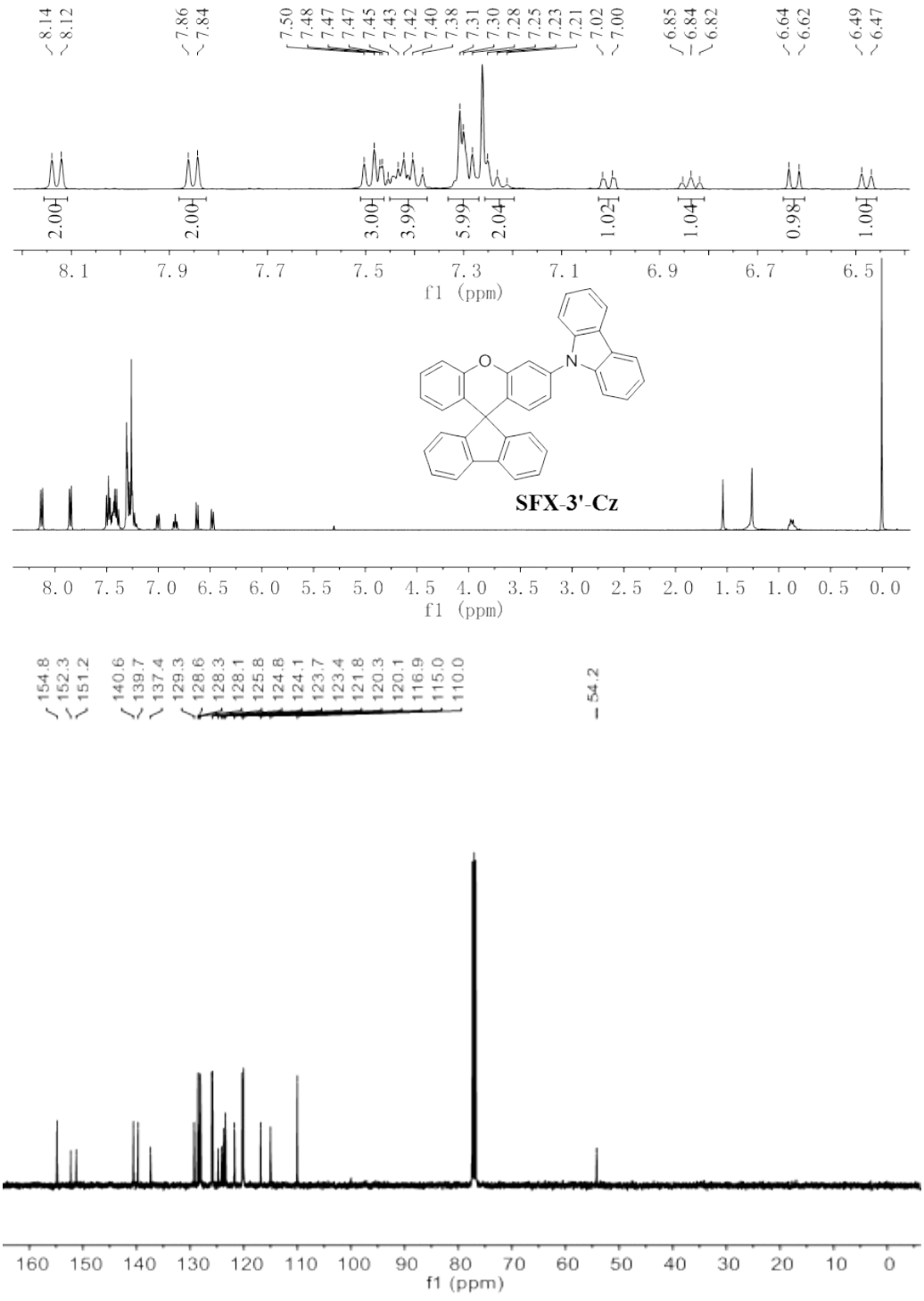


0.07mol 1,2-dichlorobenzene (8 mL) was added to a mixture of bromospiro[fluorene-9,9'-xanthene] (2.0 g, 4.86 mmol), K_2CO_3 (2.0 g, 14.47 mmol), carbazole (1.20 g, 7.18 mmol), CuI (1.40 g, 7.35 mmol), 18-Crown-6(1,4,7,10,13,16-Hexaoxacyclooctadecane) (1.90 g, 7.19 mmol) with stirred and heated at 180 ^{o}C in the dark, refluxed for 24 h under nitrogen atmosphere. The mixture was extracted with dichloromethane, then purified by column chromatography (PE：DCM=10:1). The yield of three unilateral products is about 85%.

9-(spiro[fluorene-9,9'-xanthen]-2-yl)-9H-carbazole (SFX-2-Cz). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.30 (dd, *J* = 13.8, 7.1 Hz, 3H), 7.25 – 7.17 (m, 9H), 6.88 – 6.83 (m, 2H), 6.56 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 155.2, 151.4, 140.5, 138.7, 128.7, 128.4, 128.1, 127.7, 126.5, 125.9, 124.4, 124.2, 123.4, 121.1, 120.3, 120.1, 120.0, 117.0, 54.5.



9-(spiro[fluorene-9,9'-xanthen]-3'-yl)-9H-carbazole (SFX-3'-Cz). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.48 (dd, *J* = 9.7, 5.0 Hz, 3H), 7.41 (dd, *J* = 13.6, 6.3 Hz, 4H), 7.33 – 7.27 (m, 6H), 7.26 – 7.20 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 6.9 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.3, 151.2, 140.6, 139.7, 137.4, 129.3, 128.6, 128.3, 128.1, 125.8, 124.8, 124.1, 123.7, 123.4, 121.8, 120.3, 120.1, 116.9, 115.0, 110.0, 54.2.



9-(spiro[fluorene-9,9'-xanthen]-2'-yl)-9H-carbazole (SFX-2'-Cz). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.31 (m, 4H), 7.29 (d, *J* = 10.6 Hz, 5H), 7.24 (s, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 6.50 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 151.3, 150.1, 140.5, 139.6, 132.5, 128.5, 126.5, 125.8, 124.2, 123.7, 123.1, 119.7, 118.2, 116.9, 109.6, 54.3.

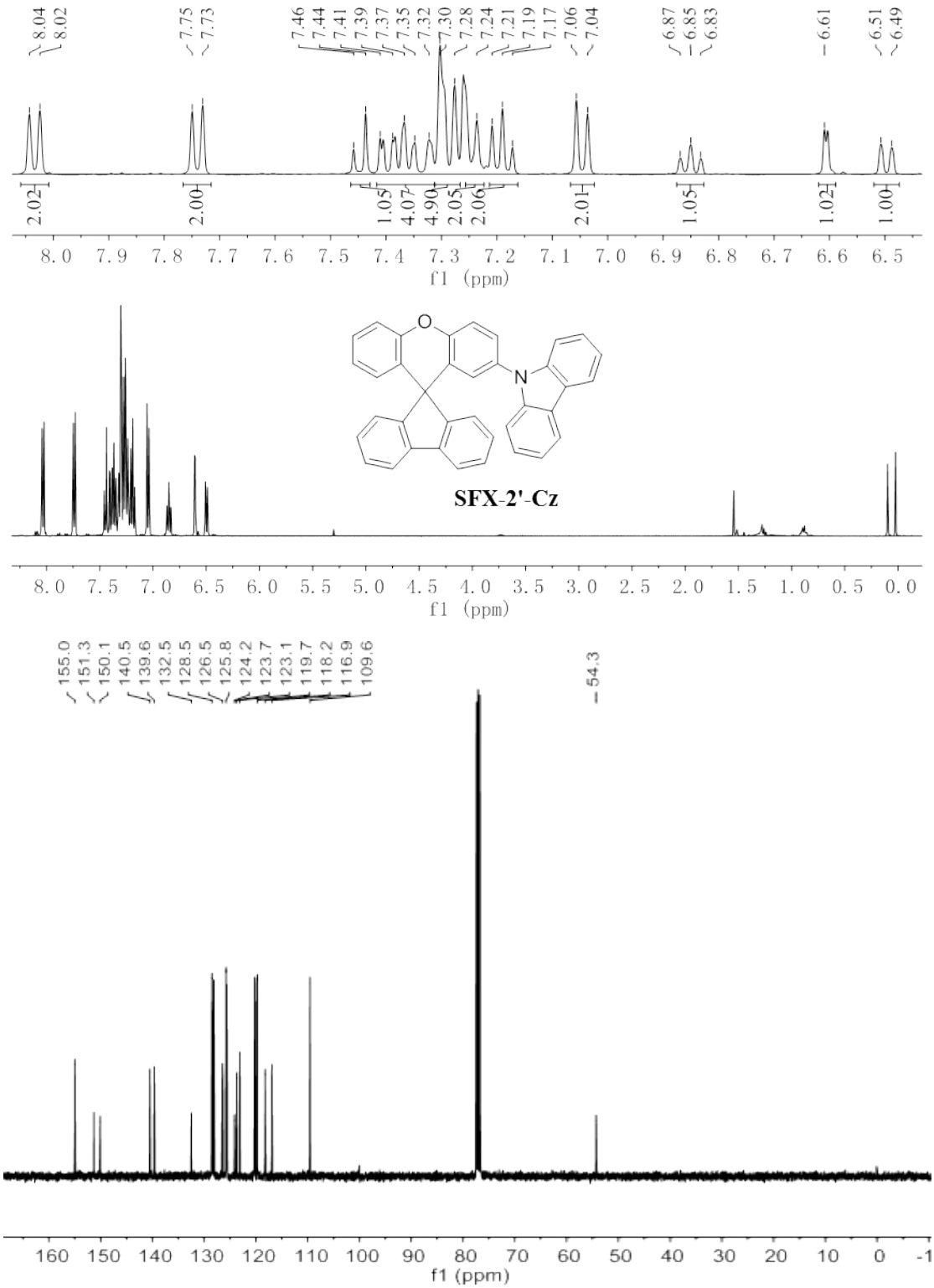


Figure S1. ^{1}H-NMR and ^{13}C-NMR spectra of three isomeric molecules of SFX-2-Cz, SFX-3'-Cz and SFX-2'-Cz.

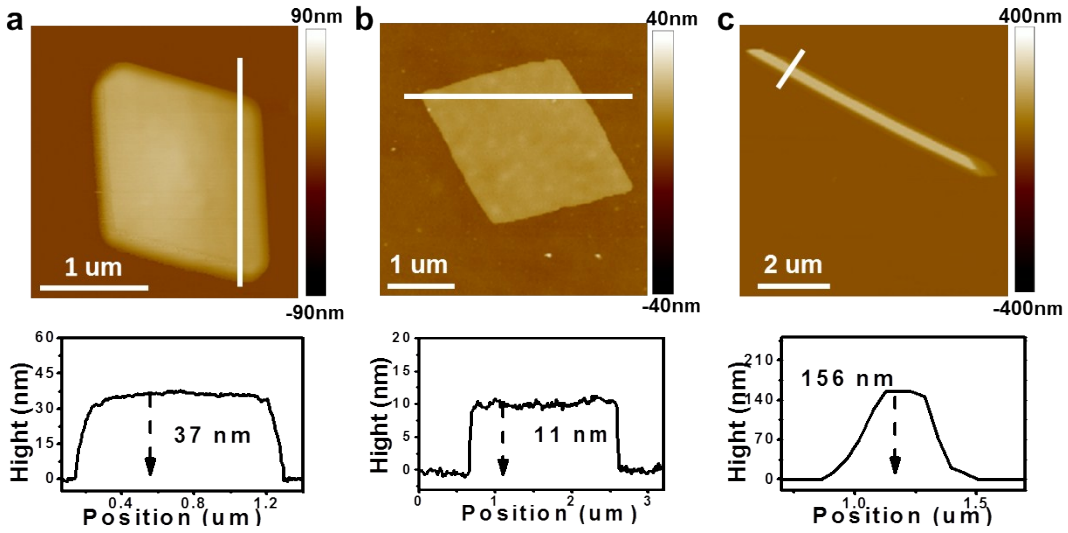


Figure S2. AFM images of a) one SFX-2-Cz parallelogram nanosheet, b) one SFX-3'-Cz rhombic nanosheet, c) one SFX-2'-Cz rod and corresponding height profile (bottom) along the white line in the images.

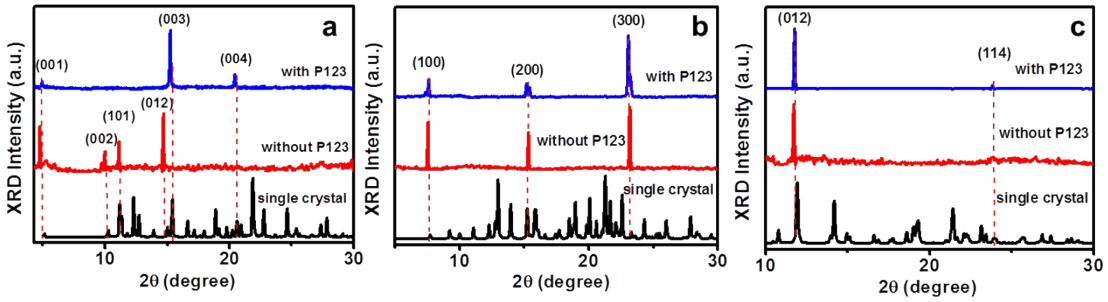


Figure S3. XRD patterns of the as-prepared a) SFX-2-Cz parallelograms, b) SFX-3'-Cz rhombuses and c) SFX-2'-Cz rods with surfactant Pluronic P123 (top), without surfactant Pluronic P123 (middle) and the standard powder spectrum based on the single crystal data by using the DIAMOND software (bottom).

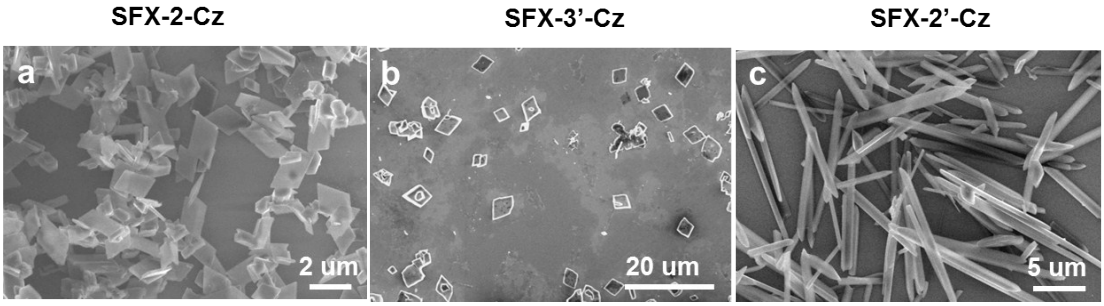


Figure S4. SEM images of the three micro/nanocrystal structures under the condition with no surfactant assistance.

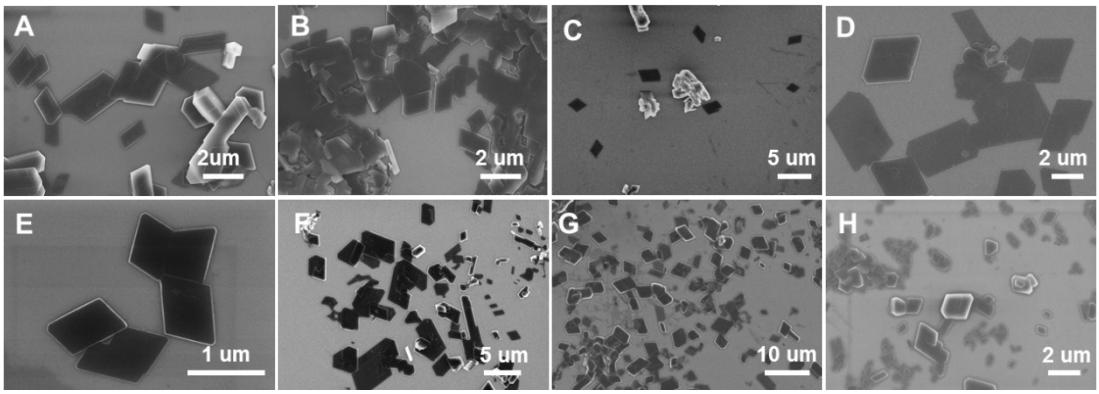


Figure S5. The corresponding SEM images of SFX-2-Cz nanosheets with different contrast experiment conditions as shown in Table S3.

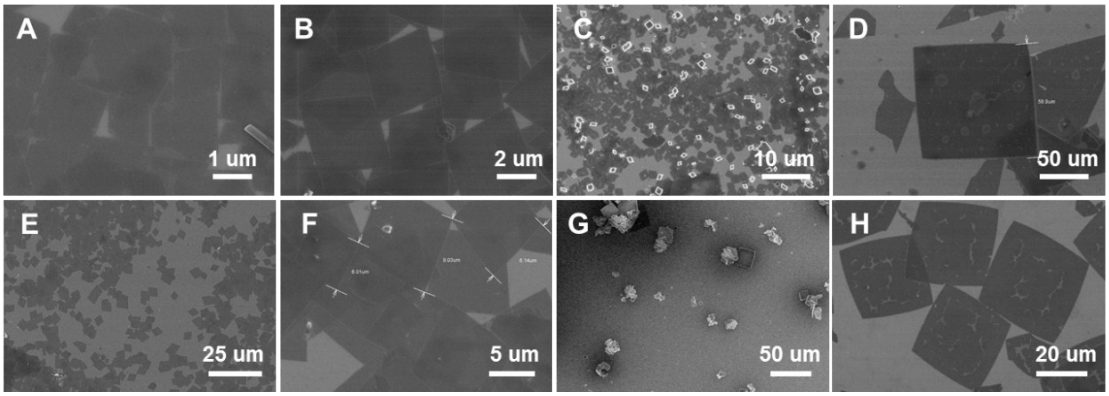


Figure S6. The corresponding SEM images of SFX-3'-Cz nanosheets with different contrast experiment conditions as shown in Table S3.

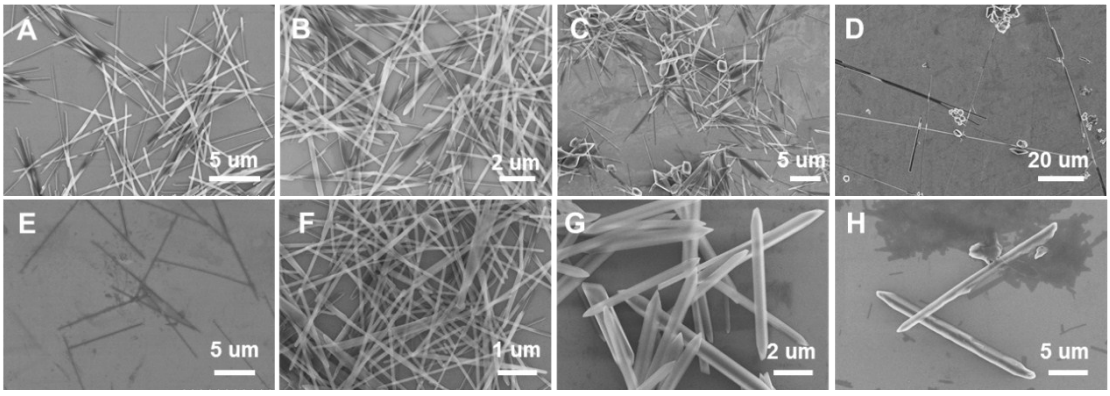


Figure S7. The corresponding SEM images of SFX-2'-Cz rods with different contrast experiment conditions as shown in Table S3.

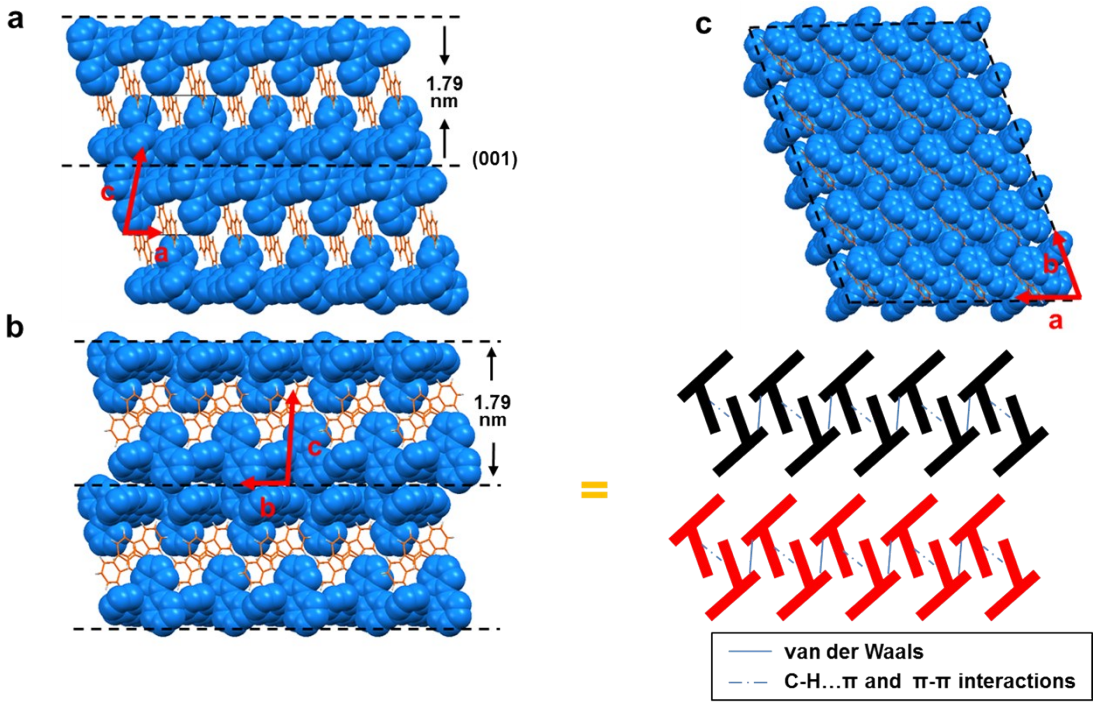


Figure S8. ILB molecular layer of SFX-2-Cz as viewed perpendicular to the: a) *ac* plane; b) *bc* plane and c) *ab* plane of the crystal lattice. (SFX groups are shown in light blue and the Cz segments are shown in orange, respectively).

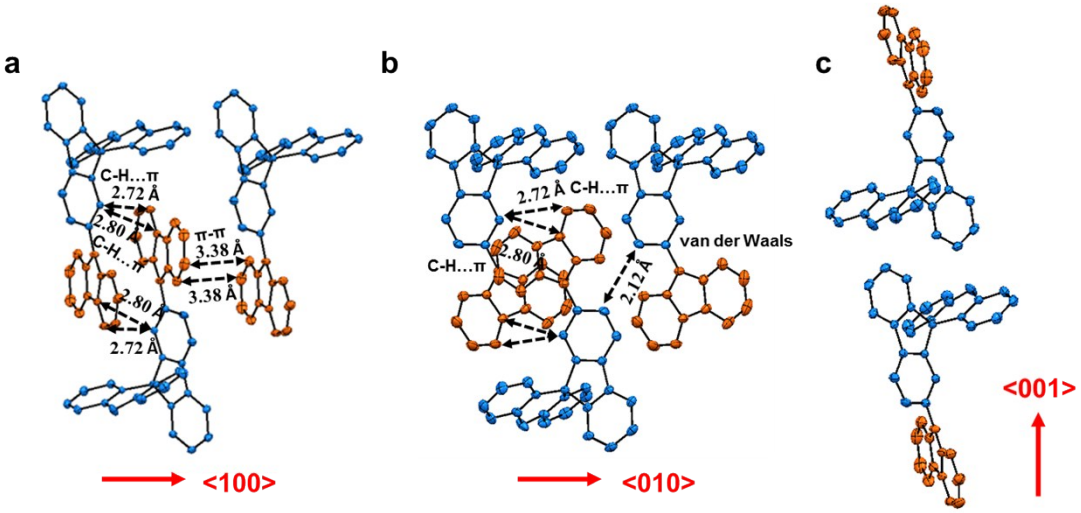


Figure S9. Molecular packing and supramolecular interactions of SFX-2-Cz in three axis directions.

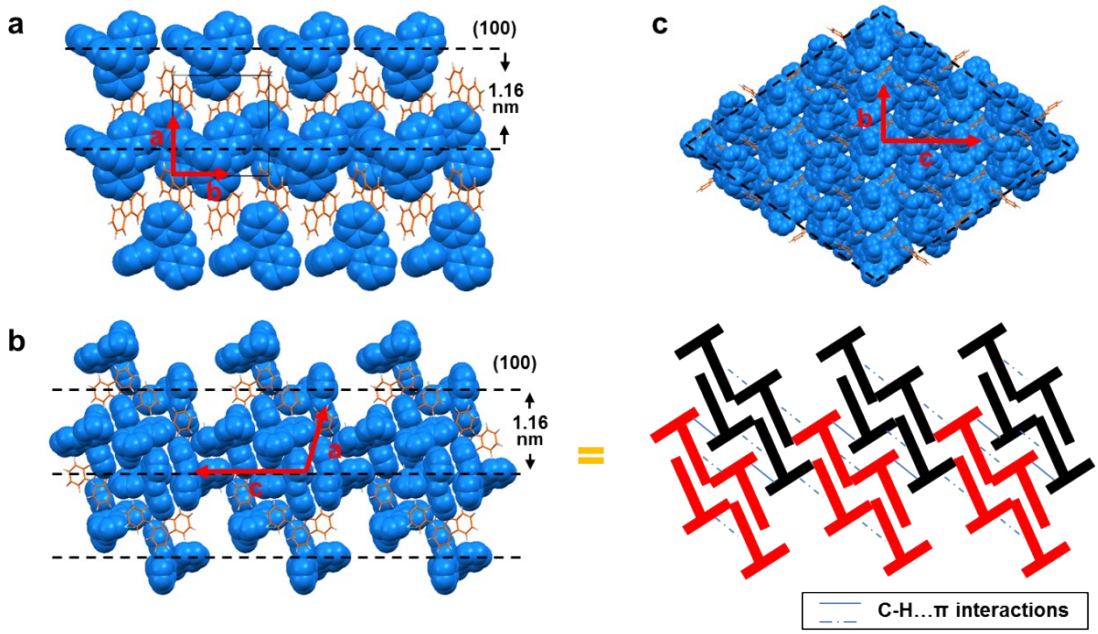


Figure S10. Molecular layer of SFX-3'-Cz viewed perpendicular to the: a) *ab* plane; b) *ac* plane and c) *bc* plane of the crystal lattice. (SFX groups are shown in light blue and the Cz segments are shown in orange, respectively).

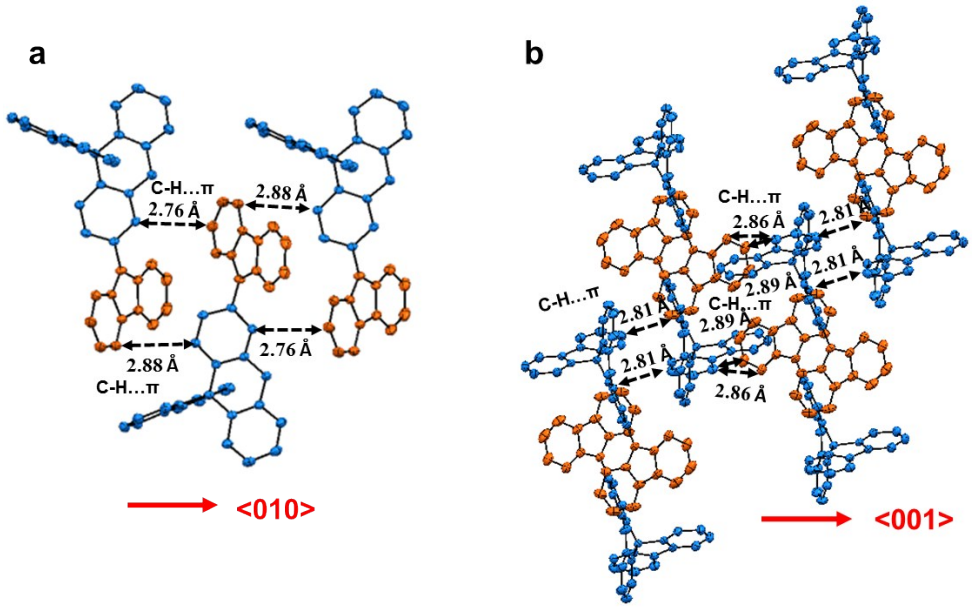


Figure S11. Molecular packing and supramolecular interactions of SFX-3'-Cz in two axis directions.

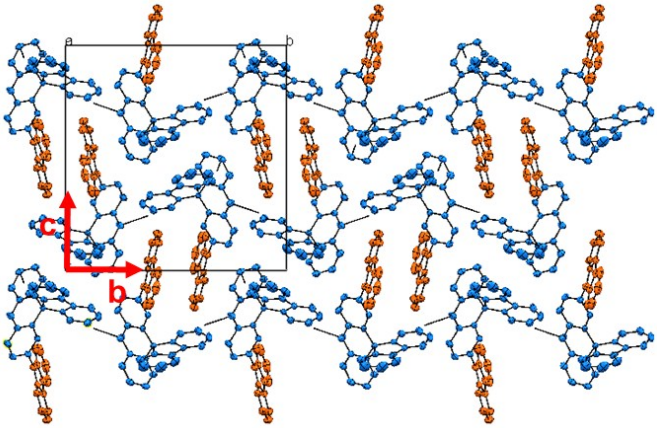


Figure S12. Molecular packing of SFX-2'-Cz viewed perpendicular to the *bc* plane.

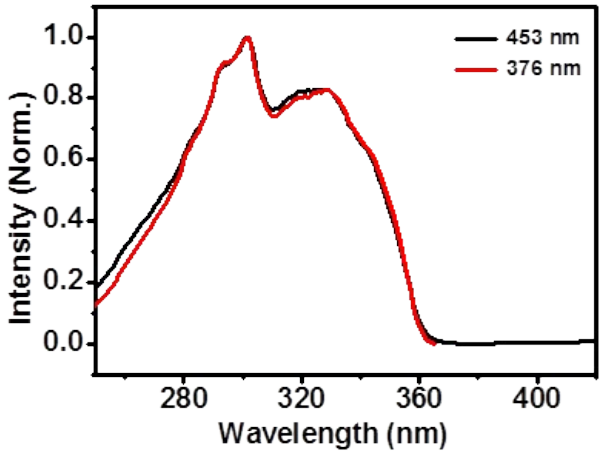


Figure S13. Excitation spectra of SFX-2-Cz nanocrystals monitored at 376 and 453 nm.

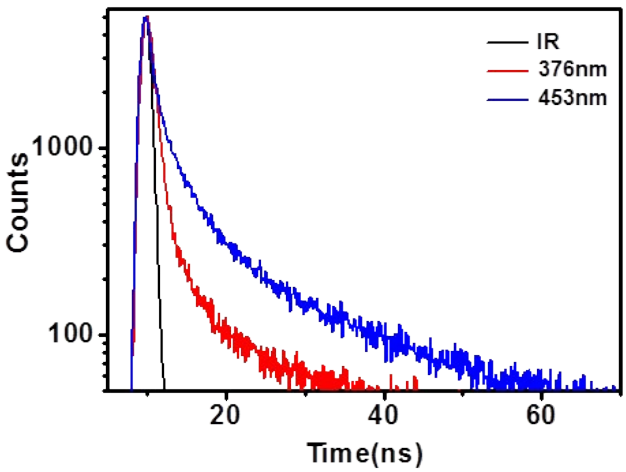


Figure S14. Transient PL decay spectra of SFX-2-Cz nanocrystals monitored at 376 and 453 nm.

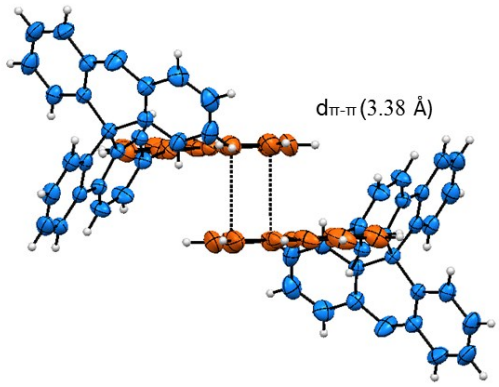


Figure S15. π-stacking between Cz segments of SFX-2-Cz moleculars.

Table S1. Single crystal data of the three moleculars

name	SFX-2-Cz	SFX-3'-Cz	SFX-2'-Cz
CCDC No.	1577085	1577086	1577084
formula	$C_{37}H_{23}NO$	$C_{37}H_{23}NO$	$C_{37}H_{23}NO$
fw[g/mol]	497.56	497.56	497.56
crystal colar	colorless	white	colorless
crystal size [mm]	0.3*0.25*0.2	0.21*0.15*0.12	0.23*0.21*0.15
T [K]	291.64	296.15	295.67
lattice type	triclinic	monoclinic	monoclinic
space group	P-1	P 1 21/n 1	P 1 21/c 1
a [Å]	8.581(2)	12.115(2)	9.4322(9)
b [Å]	9.167(2)	11.1281(19)	16.5755(16)
c [Å]	17.575(4)	19.686(3)	16.9196(15)
α [°]	89.893(6)	90	90
β [°]	79.223(7)	106.472(2)	90.836(3)
γ [°]	70.216(6)	90	90
V [Å^3]	1275.1(5)	2544.9(7)	2645.0(4)
Z	2	4	4
ρ_{calcd} [g/cm3]	1.296	1.299	1.249
F(000)	520	1040	1040
absorption coefficient [mm^{-1}]	0.077	0.077	0.074
θ range [°]	2.36-28.22	2.30-19.36	2.46-28.11
R1	0.0496	0.0517	0.0596
ωR2	0.1137	0.1136	0.1297
completeness	0.997	0.998	0.999

Table S2. Interaction energy (IE) of two dimers for SFX-2'-Cz

	Interaction	**$IE_{(Kcal/mol)}$**
Dimmer 1	C-H…π	-7.94
Dimmer 2	C-H…O	-4.13

Table S3. The synthesis conditions of three nanocrystals

	C (mM)	V_{THF} (mL)	$C_{surfactant}$ (mg/mL)	V_{H2O} (mL)	Surfactant
A	1	1	2	5	P123
B	4	1	2	5	P123
C	0.2	1.5	2	5	P123
D	0.2	3	2	5	P123
E	0.2	1	1	5	P123
F	0.2	1	4	5	P123
G	0.2	1	2	2	P123
H	0.2	1	2	8	P123

Table S4. Solvent diffusion growth conditions of three compounds

Compound	Good solvent	Poor solvent	Growth time [day]	Growth temperature [°C]
SFX-2-Cz	tetrahydrofuran	isopropanol	28	25
SFX-3’-Cz	tetrahydrofuran	isopropanol	15	25
SFX-2’-Cz	tetrahydrofuran	isopropanol	17	25