

Supporting Information

Discrete Dimeric Anthracene Stackings in Solids with Enhanced Excimer Fluorescence

Haichao Liu,^{†,‡} Dengli Cong,^{‡,‡} Bao Li,[†] Ling Ye,[†] Yunpeng Ge,[†] Xiaohui Tang,[†] Yue Shen,[†] Yating Wen,[†] Jun Wang,[†] Changjiang Zhou,[†] and Bing Yang^{,†}*

[†] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China

[‡] College of Pharmacy, Jilin University, Changchun, 130021, P. R. China

*Corresponding Author. E-mail: yangbing@jlu.edu.cn

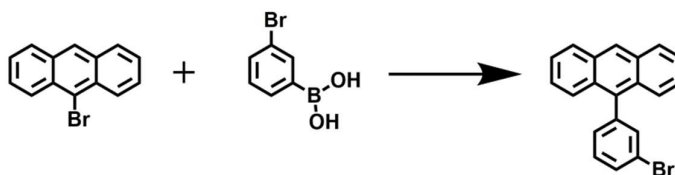
SI General informations about synthesis, crystal and photophysical measurements

SI-1 The details of synthetic procedures

General information: All the reagents and solvents used for the synthesis were purchased from Aldrich and Acros companies and used without further purification. The synthesis procedure was presented in Scheme S1 and S2. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer at 500 MHz, using tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument.

The synthesis of 9-(3-bromophenyl)anthracene (ANP-m-Br)

A mixture of (3-bromophenyl)boronic acid (1.205 g, 6.0 mmol), 9-bromoanthracene (1.285 g, 5.0 mmol), K_2CO_3 (4.416 g, 32.0 mmol), 16 mL distilled water and 24 mL toluene was degassed and recharged with nitrogen. Then $\text{Pd}(\text{PPh}_3)_4$ (173 mg, 0.15 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed at 90 °C for 48 h under nitrogen atmosphere, the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the petroleum ether and then recrystallized from the mixture of dichloromethane/methanol to afford the light yellow powder in 48% yield (800 mg). ^1H NMR (500 MHz, DMSO, 25 °C, TMS): δ = 8.73 (s, 1H), 8.18 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.58 – 7.50 (m, 4H), 7.50 – 7.43 (m, 3H); ^{13}C NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ = 141.051 (C), 135.115 (C), 134.121 (CH), 131.291 (C), 130.669 (CH), 130.071 (C), 130.002 (CH), 129.973 (CH), 128.441 (CH), 127.148 (CH), 126.420 (CH), 125.741 (CH), 125.211 (CH), 122.607 (C); MALDI-TOF MS (mass m/z): 333.24 [M^+].

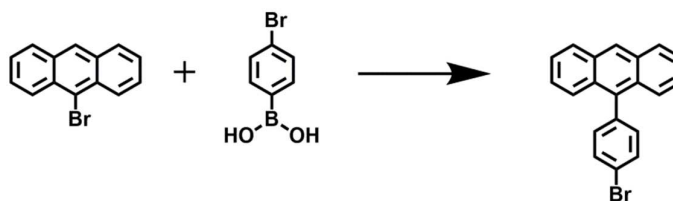


Scheme S1. Synthetic route to ANP-m-Br.

The synthesis of 9-(4-bromophenyl)anthracene (ANP-p-Br)

A mixture of (4-bromophenyl)boronic acid (623 mg, 3.1 mmol), 9-bromoanthracene (771 mg, 3.0 mmol), K_2CO_3 (2.760 g, 20.0 mmol), 10 mL distilled water and 15 mL toluene was degassed and recharged with nitrogen. Then $\text{Pd}(\text{PPh}_3)_4$ (69 mg, 0.06 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed at 90 °C

for 48 h under nitrogen atmosphere, the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the petroleum ether and then recrystallized from the mixture of dichloromethane/methanol to afford the white powder in 28% yield (280 mg). ^1H NMR (500 MHz, DMSO, 25 °C, TMS): δ = 8.72 (s, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.50 – 7.42 (m, 2H), 7.39 (d, J = 8.3 Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ = 137.749 (C), 135.454 (C), 132.982 (CH), 131.648 (CH), 131.320 (C), 130.072 (C), 128.437 (CH), 126.985 (CH), 126.433 (CH), 125.634 (CH), 125.188 (CH), 121.742 (C); MALDI-TOF MS (mass m/z): 333.95 [M^+].



Scheme S2. Synthetic route to ANP-p-Br.

SI-2 Single crystal X-ray diffraction data

General information: Single crystals of ANP-m-Br and ANP-p-Br were prepared by crystallization from dichloromethane:methanol (3:1, v/v) mixture. All single crystals were prepared at room temperature. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K α and control Software using the RAPID AUTO at 293 (\pm 2) °C. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs. All angles and distances in crystals were measured using Meccury 1.4.1 Software.

Table S1. Crystallographic data for ANP-m-Br and ANP-p-Br.

	ANP-m-Br		ANP-p-Br
	crystal B	crystal G	
crystal colour	colorless	yellow	colorless
empirical formula	$\text{C}_{20}\text{H}_{13}\text{Br}$	$\text{C}_{20}\text{H}_{13}\text{Br}$	$\text{C}_{20}\text{H}_{13}\text{Br}$
formula weight	333.21	333.21	333.21
T [K]	293(2)	293(2)	293(2)
crystal system	triclinic	triclinic	triclinic
space group	P -1	P -1	P -1
a [Å]	10.415(2)	11.351(2)	6.0449(12)
b [Å]	11.326(2)	11.641(2)	10.748(2)
c [Å]	13.360(3)	13.509(3)	12.027(2)
α [°]	74.79(3)	112.65(3)	77.82(3)
β [°]	80.52(3)	104.93(3)	83.89(3)
γ [°]	86.87 (3)	99.81(3)	79.55(3)

$V [\text{\AA}^3]$	1499.9(5)	1517.3(5)	749.3(3)
Z	4	4	2
F(000)	672.0	672.0	336.0
density [g/cm^3]	1.476	1.459	1.477
$\mu [\text{mm}^{-1}]$	2.730	2.699	2.733
reflections collected	14874	10731	7292
unique reflections	6822	5061	3348
R (int)	0.0366	0.0674	0.0556
GOF	1.027	1.059	1.058
$R_I [I > 2\sigma(I)]$	0.0483	0.0912	0.0574
$\omega R_2 [I > 2\sigma(I)]$	0.1131	0.2190	0.1337
R_I (all data)	0.0980	0.1831	0.1020
ωR_2 (all data)	0.1326	0.2755	0.1603

SI-3 Spectroscopy measurements

General information: UV-vis spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Steady-state fluorescence spectra and fluorescence lifetimes were carried out with FLS980 Spectrometer. Solutions were placed in 1 cm path length quartz cells, and crystals were fixed on the quartz plate in terms of steady-state fluorescence spectra and fluorescence lifetimes. Quantum efficiencies were measured using an integrating sphere apparatus with excitation wavelength of 370 nm.

SII Figures

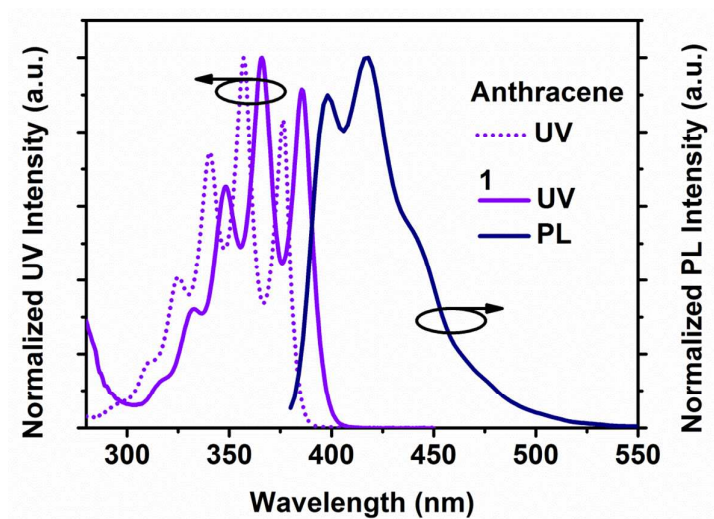


Figure S1. Absorption (anthracene and ANP-m-Br) and PL spectra (ANP-m-Br) in THF solutions.

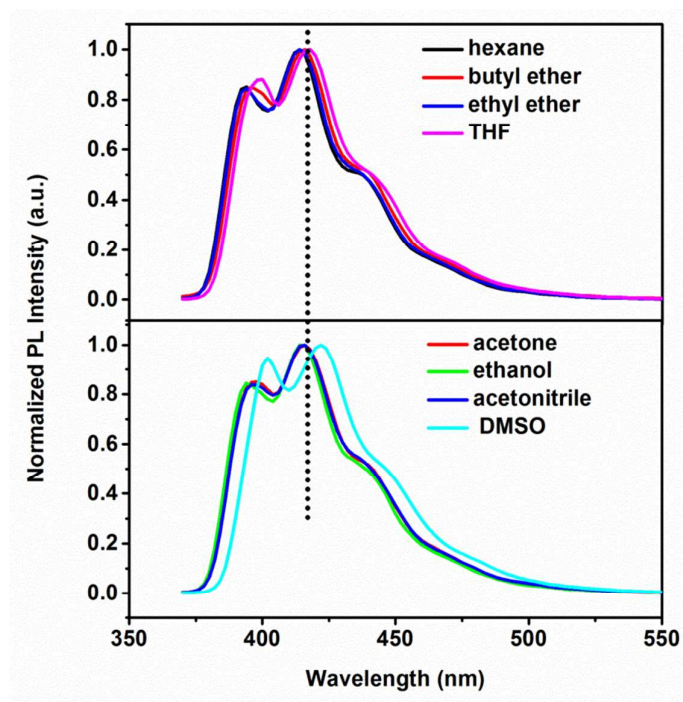


Figure S2. Solvatochromic PL spectra of ANP-m-Br in different solvents.

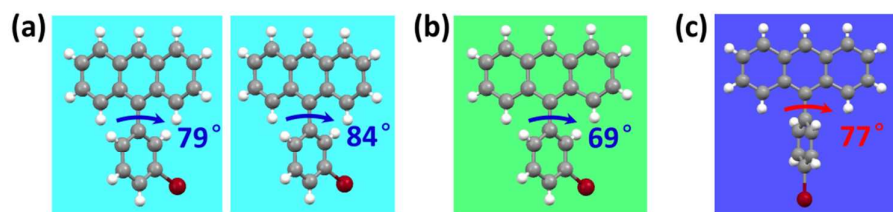


Figure S3. Two conformational structures of ANP-m-Br in crystal B (a) and crystal G (b). (c) Conformational structure of ANP-p-Br in crystal.

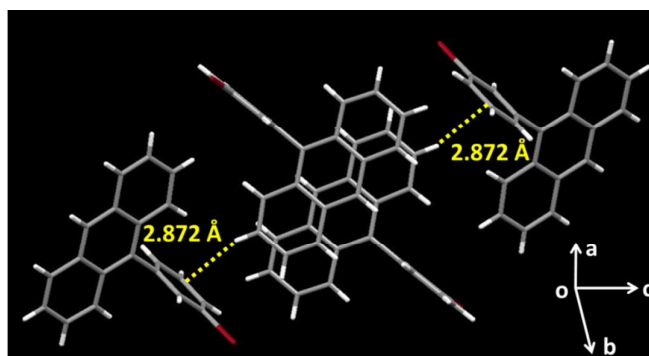


Figure S4. C-H... π interactions of ANP-m-Br in crystal B between anthracene units in dimeric structure and benzene rings of adjacent molecules.

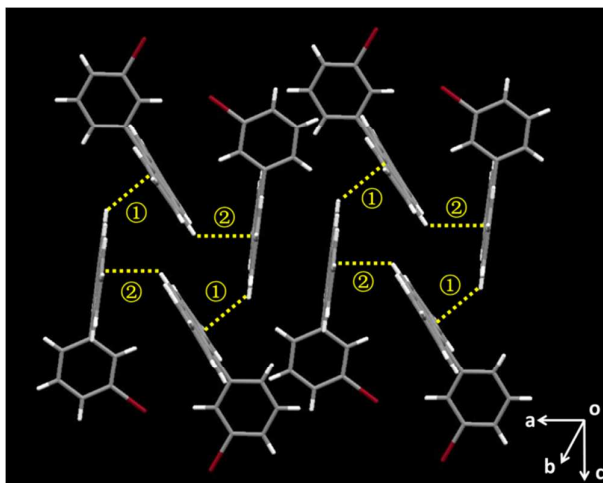


Figure S5. C-H... π interactions of ANP-m-Br in crystal B between non-dimeric anthracene units each other (①: 3.201 Å, 2.747 Å, 3.306 Å, ②: 3.346 Å, 2.739 Å, 2.925 Å).

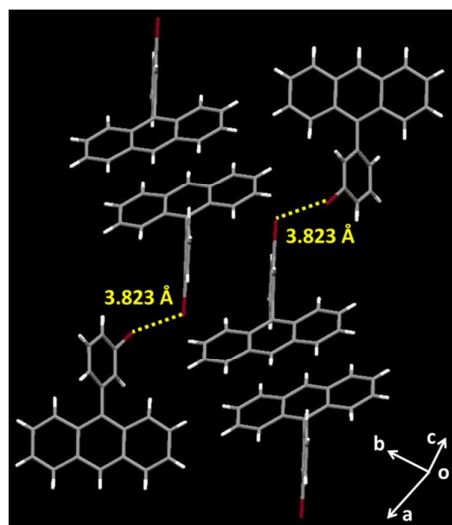


Figure S6. Br...Br interactions of ANP-m-Br in crystal G.

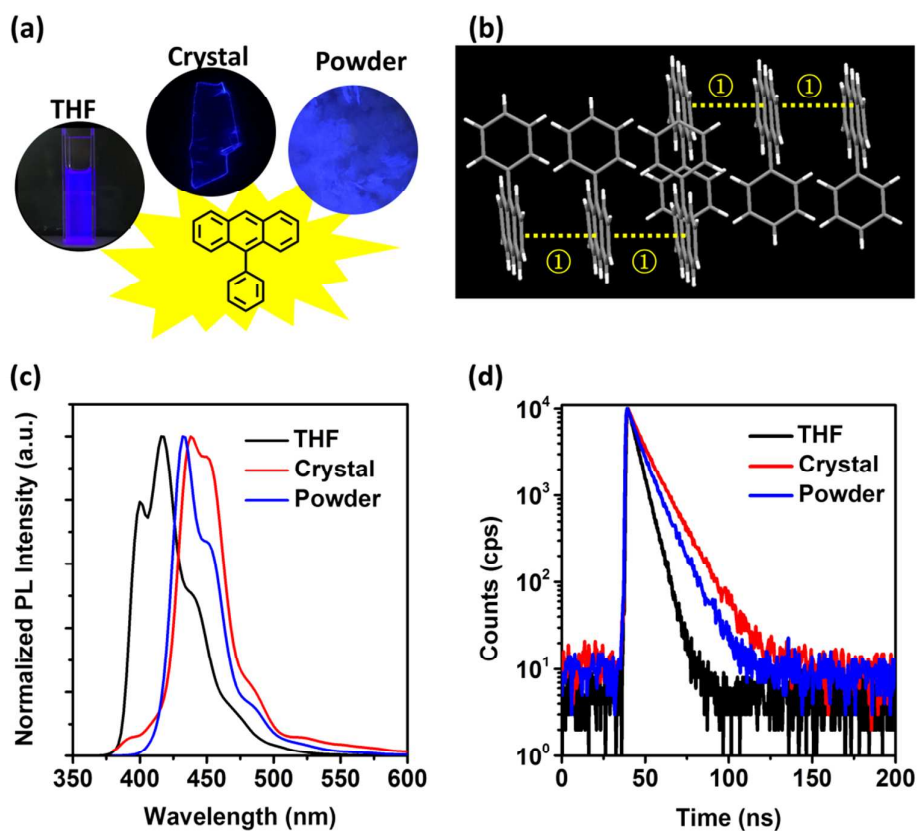


Figure S7. (a) Molecular structure of ANP and corresponding photographs in THF solution, crystal and powder under 365 nm irradiation. (b) Stacking structures of ANP in crystal (①: π - π , 3.706 Å). (c) PL spectra of ANP in THF solution ($\lambda_{\text{max}} = 416$ nm), crystal ($\lambda_{\text{max}} = 438$ nm) and powder ($\lambda_{\text{max}} = 432$ nm). (d) Time-resolved fluorescence spectra of ANP in THF solution (5.44 ns).

ns), crystal ($\tau=11.11$ ns) and powder ($\tau=8.87$ ns).

Table S1. η_{PL} values of ANP –m-Br in different solvents.

solvents	$f(\epsilon, n)^a$	ν (mPa·s) ^b	η_{PL} (%) ^c
Hexane	0.0012	0.30	10
Butyl ether	0.096	0.74	12
Ethyl ether	0.167	0.25	10
Tetrahydrofuran	0.210	0.58	16
Acetone	0.284	0.32	14
Ethanol	0.289	1.20	10
Acetonitrile	0.305	0.34	14
DMSO	0.706	2.20	50

^a f is the orientational polarizability of solvents. ^b ν is the viscosity of solvents. ^c η_{PL} is the photoluminescence quantum yield.

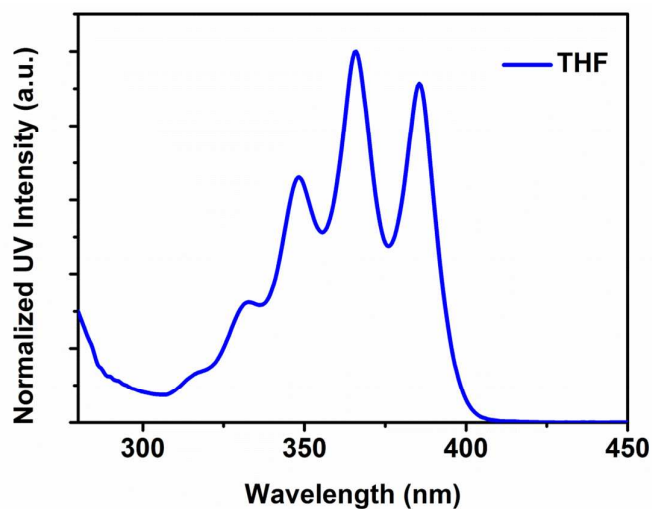


Figure S8. Absorption spectrum of ANP-p-Br in THF solution.