Electronic Supplementary Information

Competitive supramolecular assembly tunes anthracene emission over 165 nm via controlled π-overlap

Jieqiong Xu,[a] Jie Zhou,[b] Wenyan Yang,[b] Shengyong Deng[b] and Peifa Wei[b,*]

[a]*School of Chemistry and Pharmaceutical Engineering, Hefei Normal University, Hefei, Anhui, 230601, China*

[b]*Anhui Graphene Engineering Laboratory, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology, Anhui University, Hefei, Anhui 230601, China*

[*]**Authors to whom correspondence should be addressed:** pfwei@ahu.edu.cn (P. Wei)

Materials and Characterization

p-Nitrophenylboronic acid (NPBA) and 9,10-bis(pyridin-4-ylethynyl)anthracene (BPYA) were purchased from Sigma-Aldrich without further purification. All other reagents and solvents used in synthetic studies were commercially available and were used as supplied without further purification. The crystal morphology and fluorescent images were observed by a Nikon Ni-U Fluorescence Microscope with an excitation wavelength of 365 nm. The photoluminescence spectra were recorded on a spectrofluorometer FS 5. The lifetime was measured on a Horiba Fluoro max plus equipped with a xenon arc lamp (Xe900). The single crystal X-ray diffraction (XRD) patterns of all as-prepared samples were collected by X-ray diffractometer (Japan Rigaku D/MAX-γA) with Cu-Kα radiation (λ = 0.154 nm). The powder XRD spectra were collected from a D2 PHASER X-ray diffractometer over the range 5-40°.

Preparations of Five Crystals

For HB-C1, 3.4 mg NPBA and 7.6 mg BPYA were dissolved in 0.5 mL dichloromethane (DCM) in a 3 mL vial by ultrasound, then the vial was placed in a 20 mL vial with 2 mL *n*-hexane (*n*-Hex). After standing 24 h at room temperature, red crystals were obtained, washed with *n*-Hex and dried in air.

For HB-C2, 6.7 mg NPBA and 7.6 mg BPYA were dissolved in 0.5 mL trichloromethane (TCM) in a 3 mL vial by ultrasound, then the vial was placed in a 20 mL vial with 2 mL *n*-Hex. After standing 24 h at room temperature, orange-red crystals were obtained, washed with *n*-Hex and dried in air.

For BN-C1, 10.0 mg NPBA and 3.8 mg BPYA were dissolved in 0.5 mL TCM in a 3 mL vial by ultrasound, then the vial was placed in a 20 mL vial with 2 mL diethyl ether (Et_2O). After standing

24 h at room temperature, yellow-green crystals were obtained, washed with *n*-Hex and dried in air.

For BN-C2, 10.0 mg NPBA and 7.6 mg BPYA were dissolved in 0.5 mL DCM in a 3 mL vial by ultrasound, then the vial was placed in a 20 mL vial with 2 mL cyclohexane (CH). After standing 24 h at room temperature, orange-red crystals were obtained, washed with *n*-Hex and dried in air.

For BN-C3, 6.7 mg NPBA and 7.6 mg BPYA were dissolved in 0.5 mL DCM in a 3 mL vial by ultrasound, then the vial was placed in a 20 mL vial with 2 mL isopropyl ether (IE). After standing 24 h at room temperature, deep red crystals were obtained, washed with *n*-Hex and dried in air.

Calculations

The electrostatic potential (ESP) diagram based on single-crystal structure was obtained by the Multiwfn software and plotted through VMD software. Hirshfeld surface (HS) analysis through Crystal Explorer was employed to analyze intermolecular interactions in hosts based on the crystal structures. Interatomic contacts highlighted in red on the color-coded Hirshfeld surface indicated distances shorter than the sum of the van der Waals radii of the two contact atoms, while white denoted contacts close to the van der Waals distance and blue represented longer contacts.

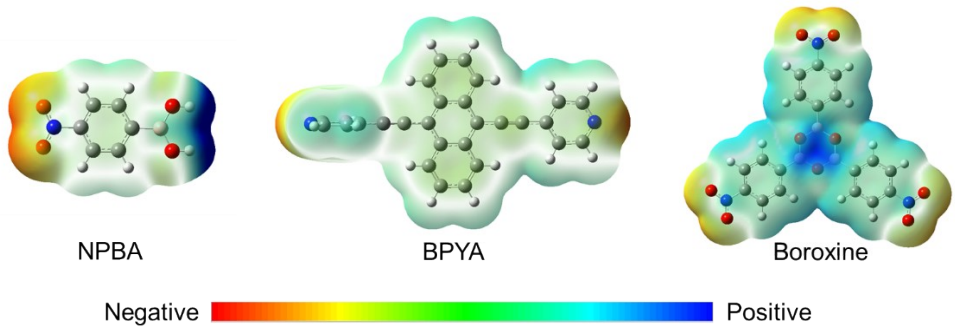

Figure S1. Electrostatic potential (ESP) maps of NPBA, BPYA and boroxine.

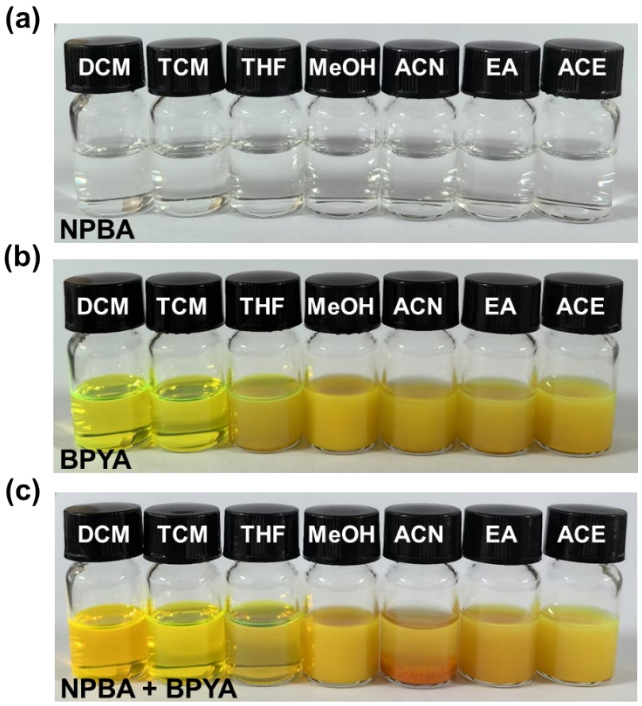

Figure S2. Photographs of (a) NPBA powder, (b) BPYA powder, and (c) their mixed powder dissolved in seven common organic solvents: dichloromethane (DCM), chloroform (TCM), tetrahydrofuran (THF), methanol (MeOH), acetonitrile (ACN), ethyl acetate (EA), and acetone (ACE).

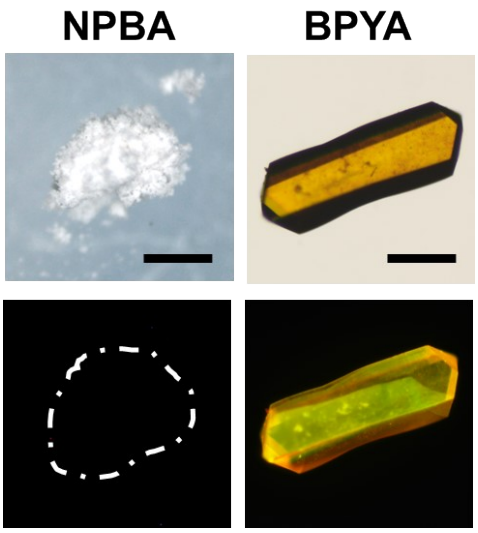

Figure S3. Optical photographs of the NPBA and BPYA under visible light (top) and UV light (bottom).

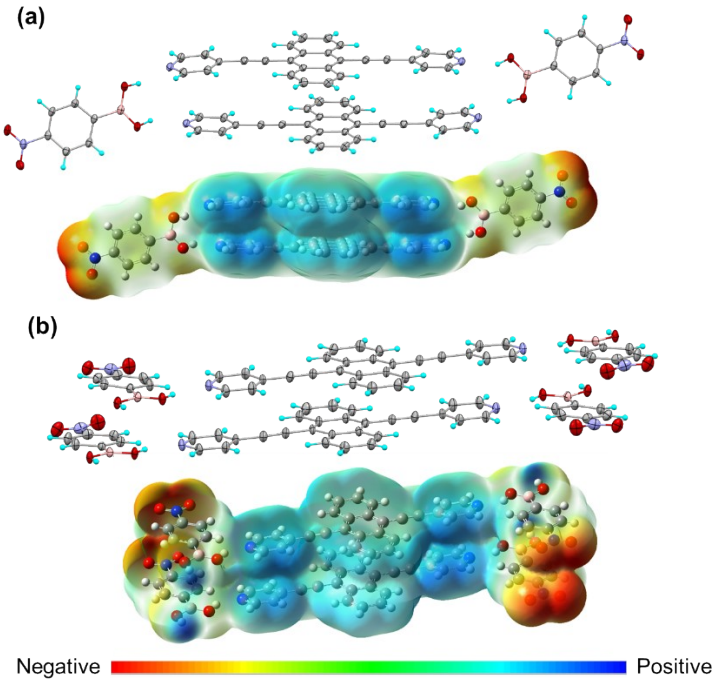

Figure S4. ORTEP representation of the X-ray structure and ESP map of (a) HB-C1 and (b) HB-C2. Color code: C, gray; H, cyan; B, light pink; O, red; N, light blue.

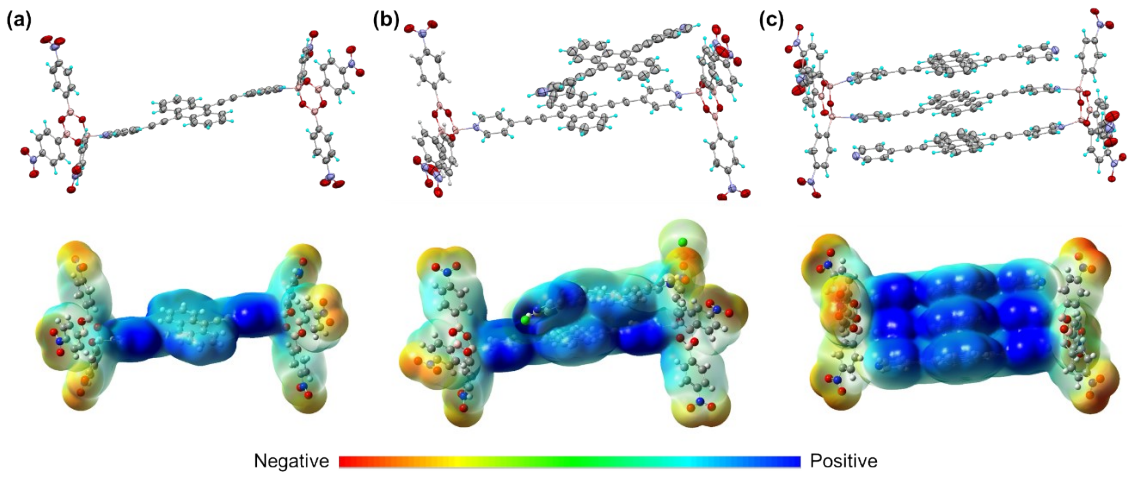

Figure S5. ORTEP representation of the X-ray structure and ESP map of (a) BN-C1, (b) BN-C2 and (c) BN-C3. Color code: C, gray; H, cyan; B, light pink; O, red; N, light blue.

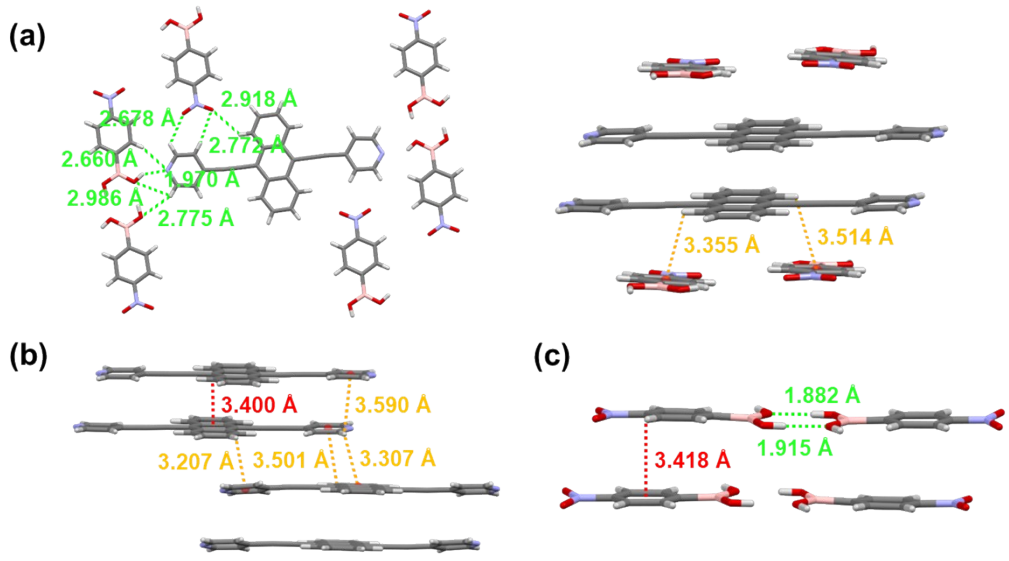

Figure S6. (a) Intermolecular interactions between NBPA and BPYA molecules in HB-C2. (b) Molecular interactions between BPYA molecules in HB-C2. (c) Molecular interactions between NBPA molecules in HB-C2.

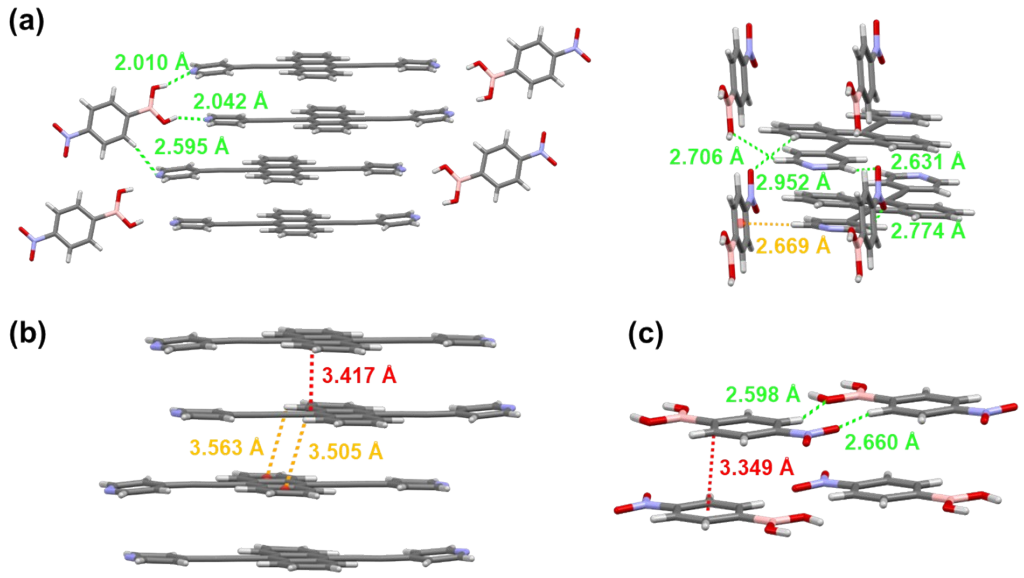

Figure S7. (a) Intermolecular interactions between NBPA and BPYA molecules in HB-C1. (b) Molecular interactions between BPYA molecules in HB-C1. (c) Molecular interactions between NBPA molecules in HB-C1. Hydrogen-bonding, green dash lines; π-π stacking, red dash lines; C-H···π interactions, yellow dash lines. C, grey; H, white; B, light pink; O, red; N, light blue.

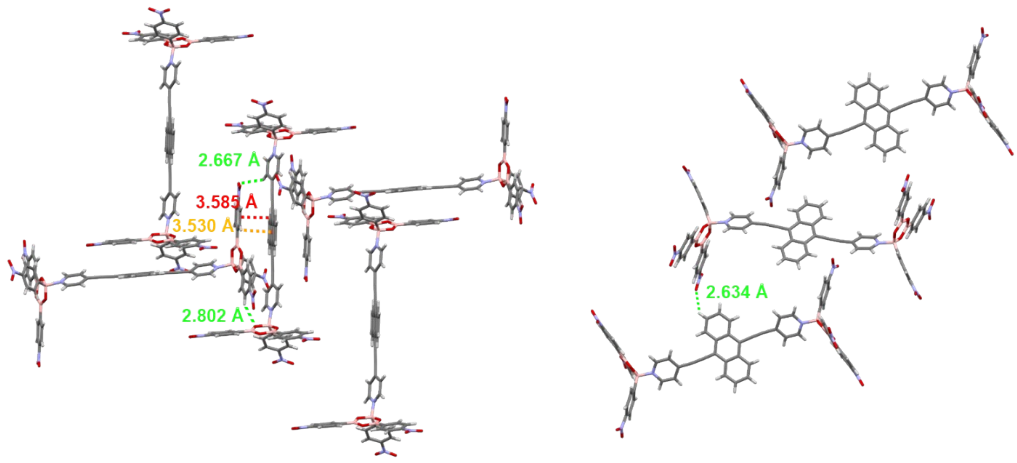

Figure S8. Intermolecular interactions in BN-C1. Hydrogen-bonding interactions, green dash lines; π-π interactions, red dash lines; C-H···π interactions, yellow dash lines.

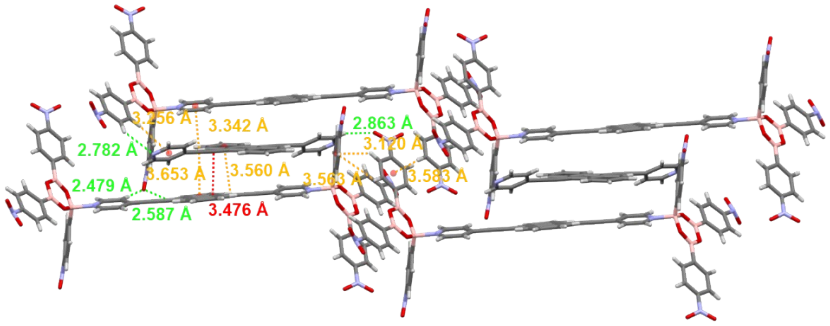

Figure S9. Intermolecular interactions in BN-C2. Hydrogen-bonding interactions, green dash lines; π-π interactions, red dash lines; C-H···π interactions, yellow dash lines.

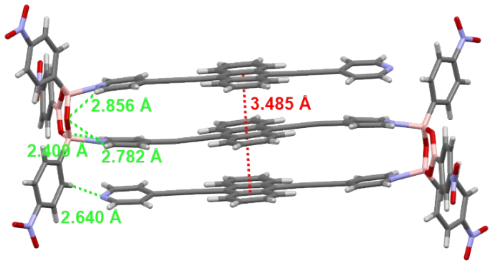

Figure S10. Intermolecular interactions in BN-C2. Hydrogen-bonding interactions, green dash lines; π-π interactions, red dash lines; C-H···π interactions, yellow dash lines.

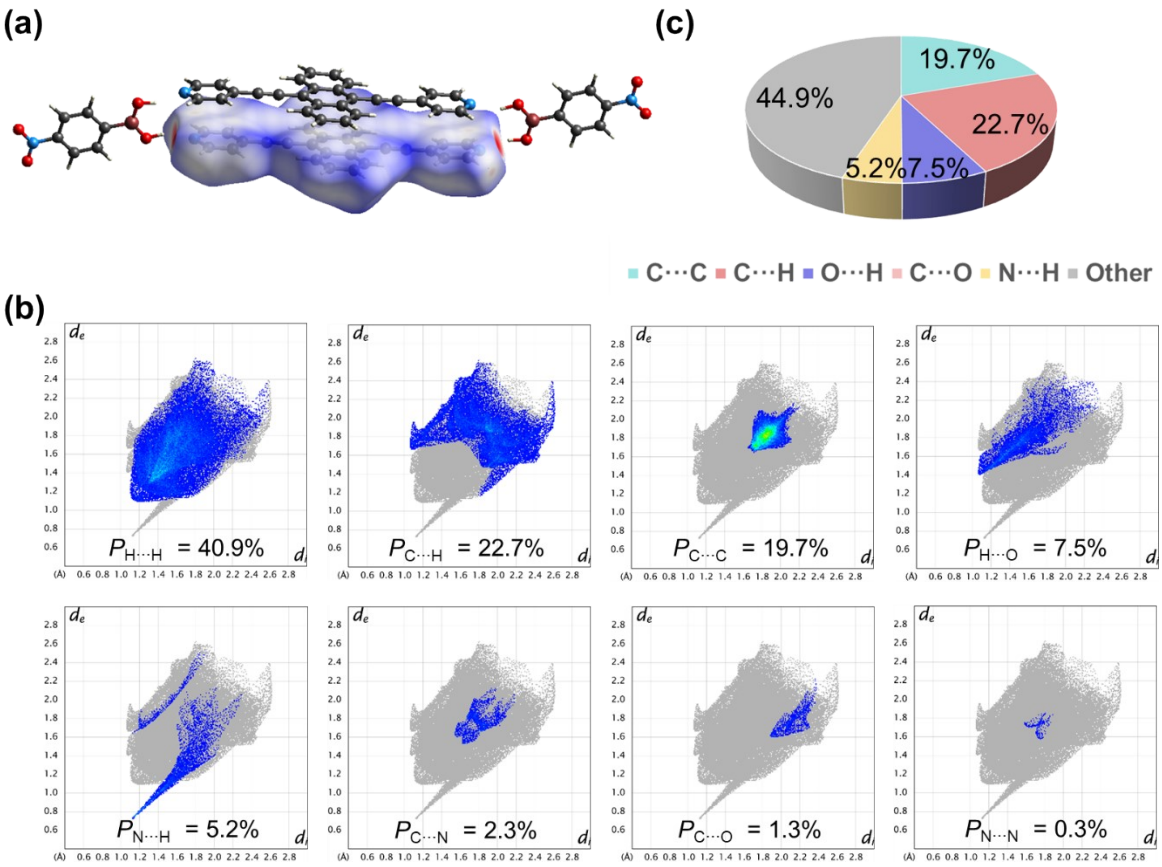

Figure S11. (a) Hirshfeld surfaces analysis (mapped over d_{norm}) and (b) decomposed fingerprint plots of HB-C1. Full fingerprints appeared as grey shadows underneath decomposed plots, and selected intermolecular interactions were shown as a blue shadow. (c) Proportions of intermolecular C···C, C···H, O···H, C···O, N···H and other interactions to the total intermolecular interactions based on the crystal structure.

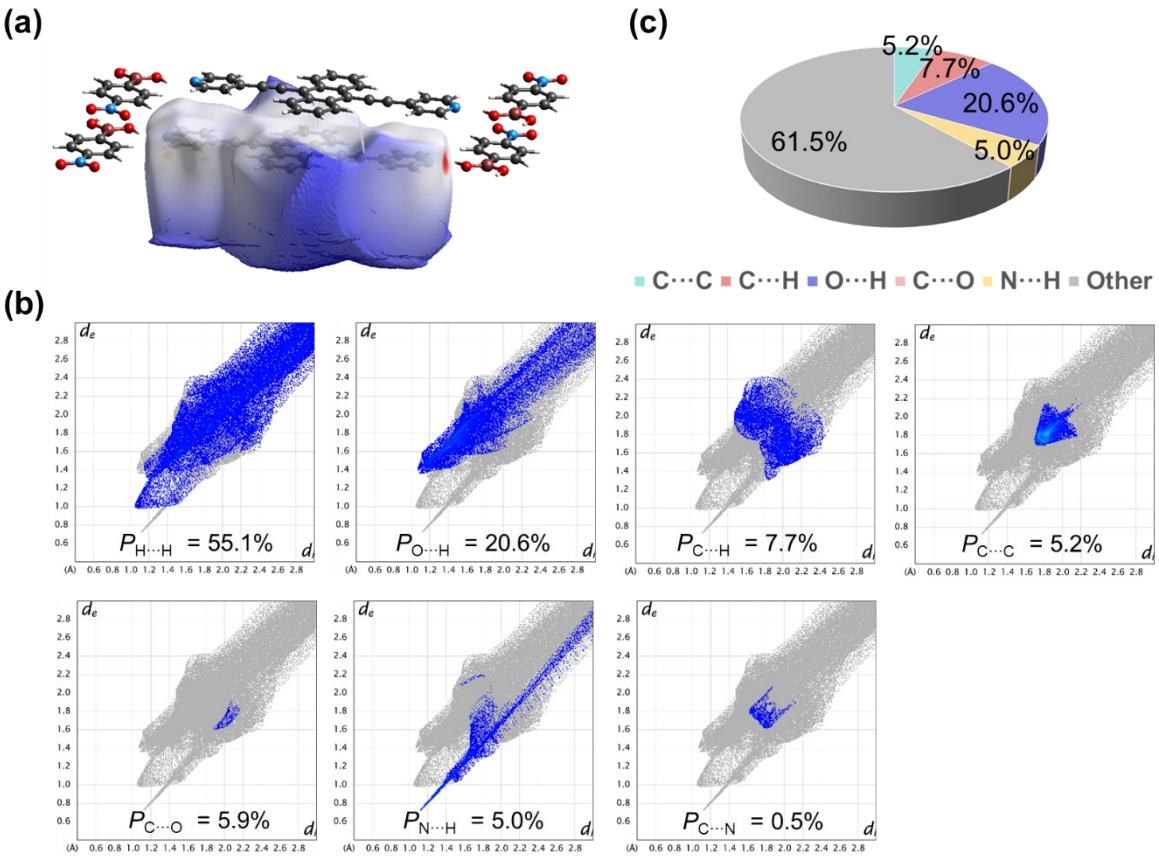

Figure S12. (a) Hirshfeld surfaces analysis (mapped over d_{norm}) and (b) decomposed fingerprint plots of HB-C2. Full fingerprints appeared as grey shadows underneath decomposed plots, and selected intermolecular interactions were shown as a blue shadow. (c) Proportions of intermolecular C···C, C···H, O···H, C···O, N···H and other interactions to the total intermolecular interactions based on the crystal structure.

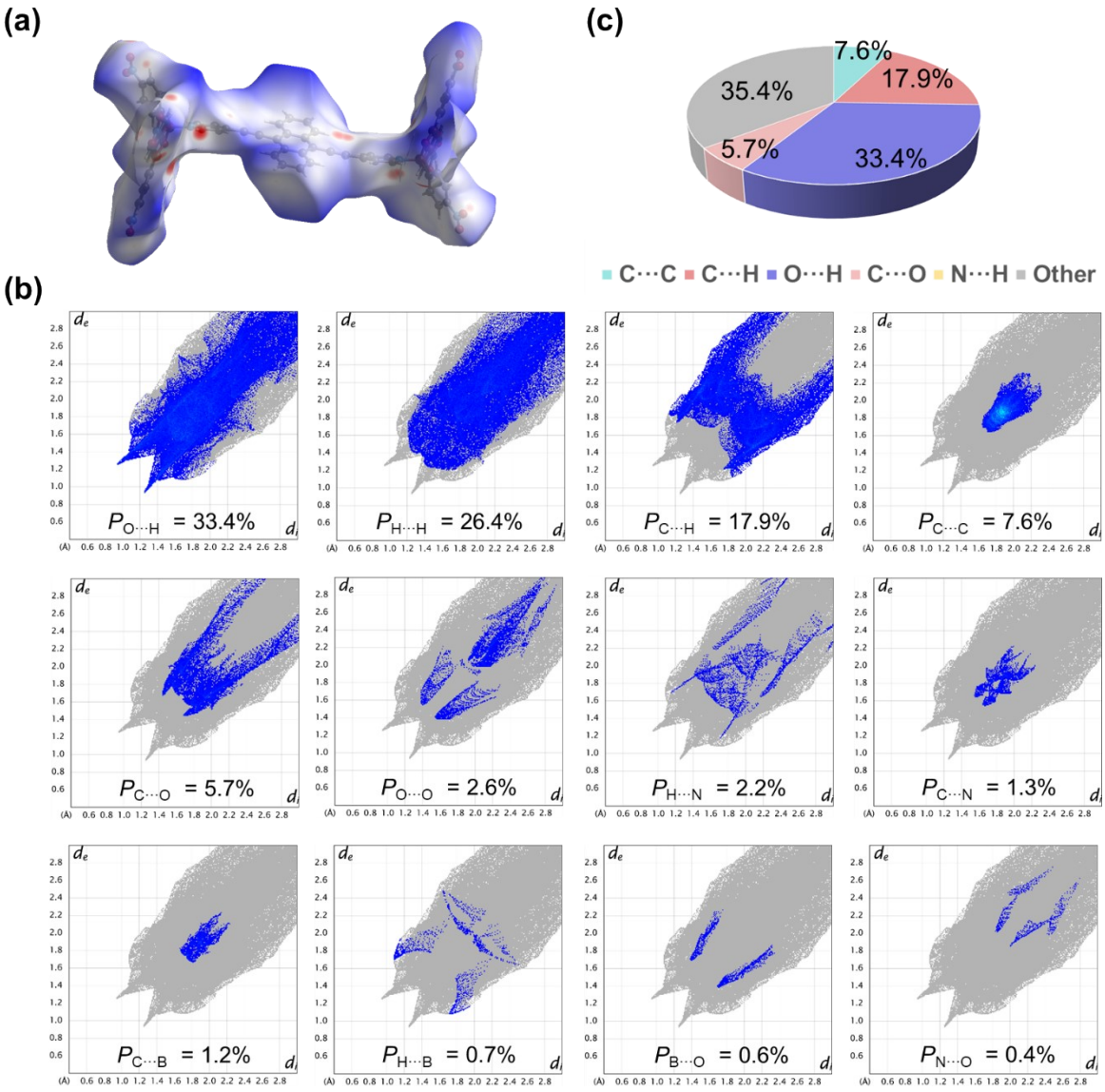

Figure S13. (a) Hirshfeld surfaces analysis (mapped over d_{norm}) and (b) decomposed fingerprint plots of BN-C1. Full fingerprints appeared as grey shadows underneath decomposed plots, and selected intermolecular interactions were shown as a blue shadow. (c) Proportions of intermolecular C···C, C···H, O···H, C···O, N···H and other interactions to the total intermolecular interactions based on the crystal structure.

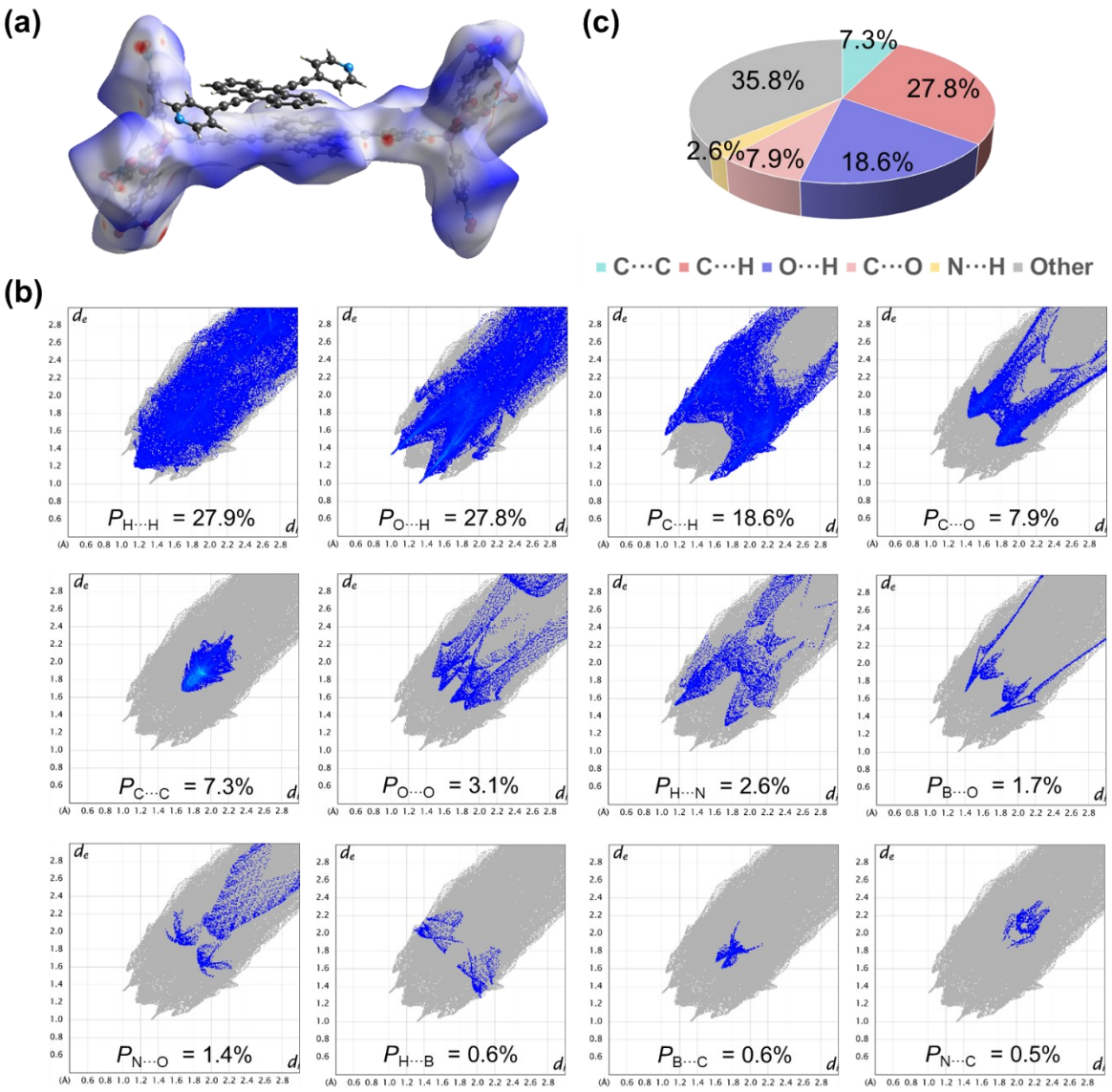

Figure S14. (a) Hirshfeld surfaces analysis (mapped over d_{norm}) and (b) decomposed fingerprint plots of BN-C2. Full fingerprints appeared as grey shadows underneath decomposed plots, and selected intermolecular interactions were shown as a blue shadow. (c) Proportions of intermolecular C···C, C···H, O···H, C···O, N···H and other interactions to the total intermolecular interactions based on the crystal structure.

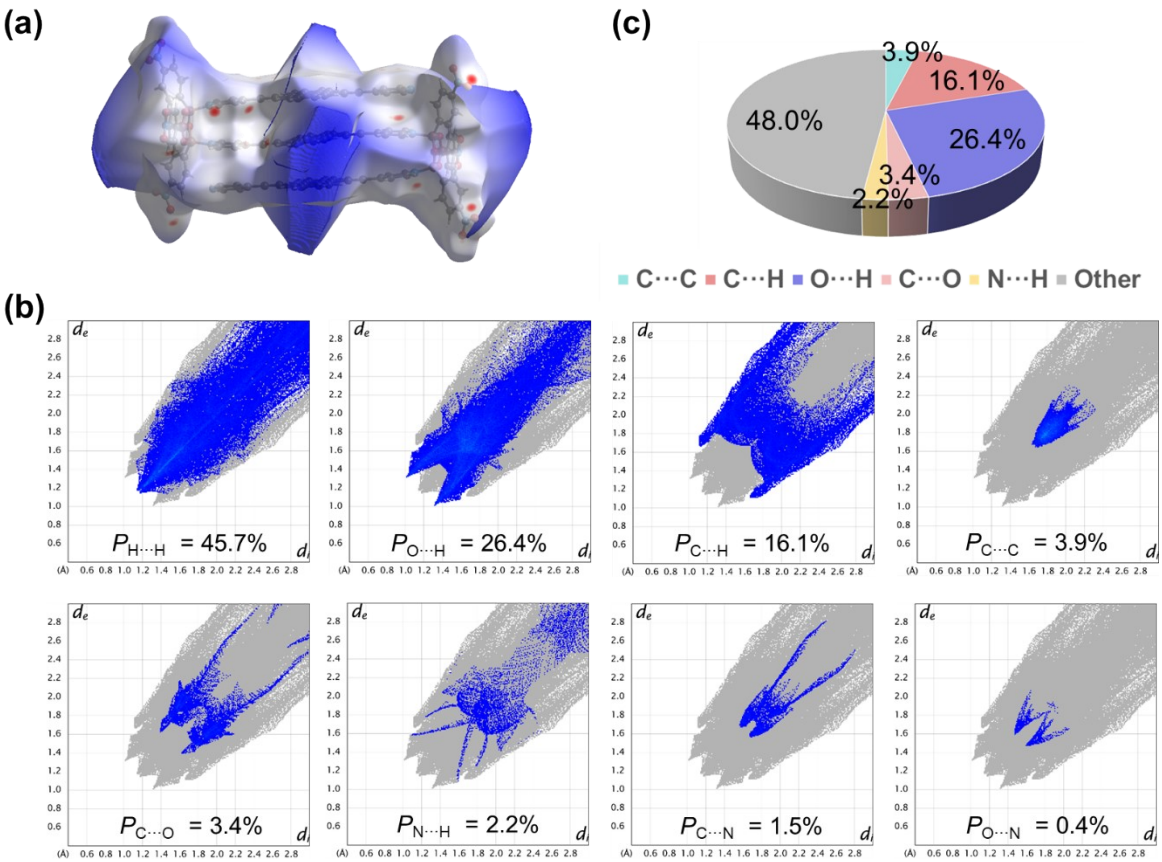

Figure S15. (a) Hirshfeld surfaces analysis (mapped over d_{norm}) and (b) decomposed fingerprint plots of BN-C3. Full fingerprints appeared as grey shadows underneath decomposed plots, and selected intermolecular interactions were shown as a blue shadow. (c) Proportions of intermolecular C···C, C···H, O···H, C···O, N···H and other interactions to the total intermolecular interactions based on the crystal structure.

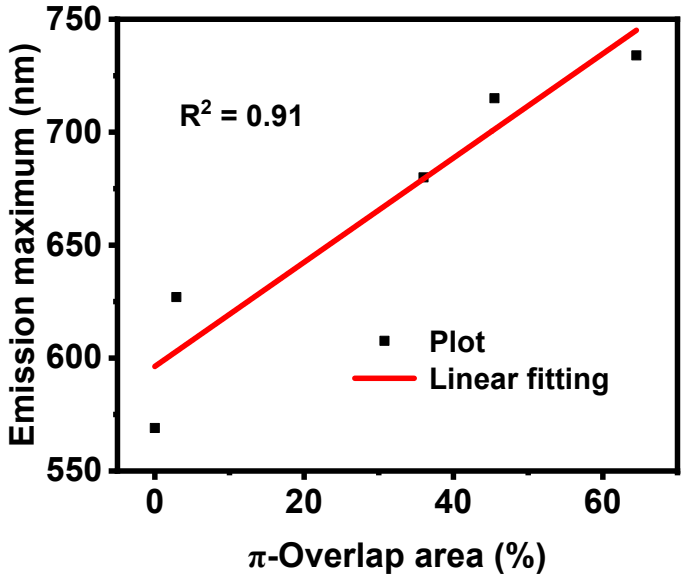

Figure S16. The linear relationship between emission maximum and π-overlap area of five crystals.

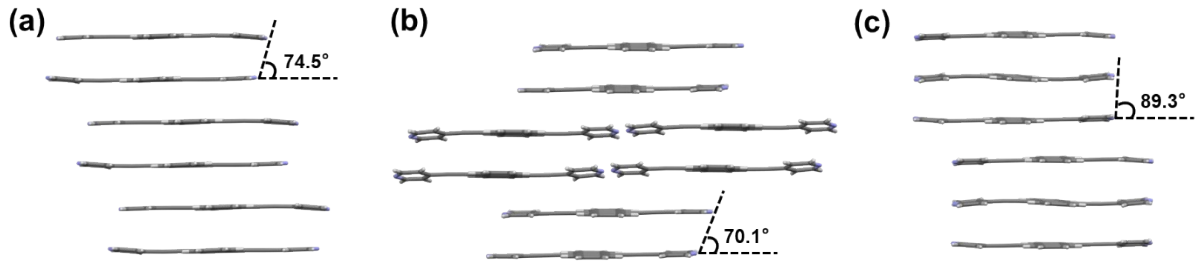

Figure S17. Molecular packing of BPYA in (a) HB-C1, (b) HB-C2 and (c) BN-C3, respectively.

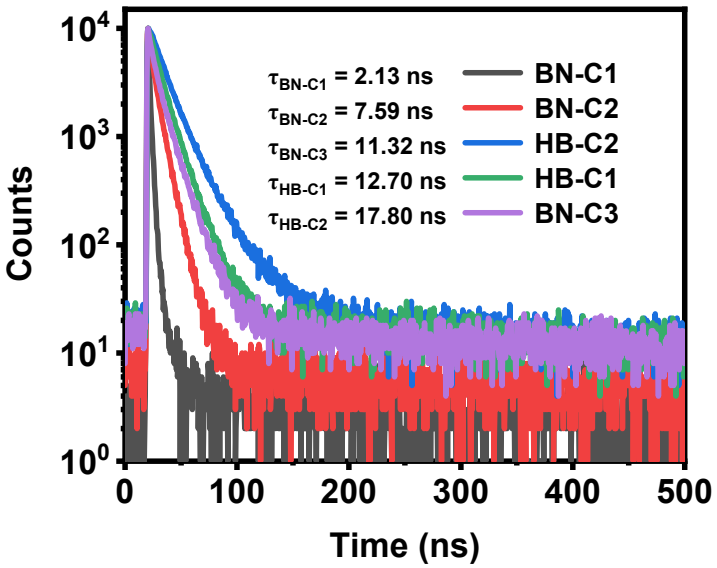

Figure S18. Time-resolved fluorescence decay profiles for five crystals.

Table S1. Specific parameters for the preparation of the five crystalline phases by vapor diffusion method.

Crystal	Solvent System	NPBA : BPYA Ratio	Temperature	Growth time
HB-C1	DCM/*n*-Hex	1 : 1	25 °C	24 h
HB-C2	TCM/*n*-Hex	2 : 1	25 °C	24 h
BN-C1	TCM/Et_2O	6 : 1	25 °C	24 h
BN-C2	DCM/CH	3 : 1	25 °C	24 h
BN-C3	DCM/IE	1 : 2	25 °C	24 h

Table S2. Crystal data and structure refinement for HB-C1.

Crystal	HB-C1
Empirical formula	$C_{34}H_{22}BN_3O_4$
Formula weight	547.36
Temperature/K	298
Crystal system	Triclinic
Space group	P -1
a/Å	7.28717
b/Å	9.78487
c/Å	9.0201
α/°	95.9830
β/°	93.9279
γ/°	97.9149
Volume/Å^3	1331.24
Z	2
ρ_{calc}/g cm^{-3}	1.366
μ/mm^{-1}	0.728
F(000)	568.0
R_1/%	5.49
CCDC number	2524883

Table S3. Crystal data and structure refinement for HB-C2.

Crystal	HB-C2
Empirical formula	$C_{42}H_{30}B_2Cl_6N_4O_8$
Formula weight	953.02
Temperature/K	120
Crystal system	Triclinic
Space group	P -1
a/Å	13.4057
b/Å	15.8559
c/Å	20.9632
α/°	99.4547
β/°	99.8780
γ/°	94.9948
Volume/Å^3	4299.67
Z	4
ρ_{calc}/g cm^{-3}	1.472
μ/mm^{-1}	4.135
F(000)	1944.0
R_1/%	9.82
CCDC number	2524901

Table S4. Crystal data and structure refinement for BN-C1.

Crystal	BN-C1
Empirical formula	$C_{34}H_{22}B_3Cl_6N_4O_9$
Formula weight	875.68
Temperature/K	120
Crystal system	Orthorhombic
Space group	P b c a
a/Å	15.12783
b/Å	19.4966
c/Å	25.6114
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7553.8
Z	8
ρ_{calc}/g cm^{-3}	1.540
μ/mm^{-1}	0.635
F(000)	3544.0
R_1/%	5.31
CCDC number	2524885

Table S5. Crystal data and structure refinement for BN-C2.

Crystal	BN-C2
Empirical formula	$C_{97}H_{66}B_6Cl_{10}N_{10}O_{18}$
Formula weight	2078.95
Temperature/K	150
Crystal system	Triclinic
Space group	P -1
a/Å	9.7883
b/Å	12.3872
c/Å	21.4954
α/°	105.172
β/°	93.698
γ/°	106.045
Volume/Å^3	2391.02
Z	1
ρ_{calc}/g cm^{-3}	1.444
μ/mm^{-1}	3.288
F(000)	1062.0
R_1/%	9.26
CCDC number	2524859

Table S6. Crystal data and structure refinement for BN-C3.

Crystal	BN-C3
Empirical formula	$C_{149}H_{140}B_6Cl_2N_{12}O_{19}$
Formula weight	2538.48
Temperature/K	120
Crystal system	Monoclinic
Space group	P 2_1/n
a/Å	10.8640
b/Å	18.0411
c/Å	36.2165
α/°	90
β/°	95.724
γ/°	90
Volume/Å^3	7063.0
Z	2
ρ_{calc}/g cm^{-3}	1.194
μ/mm^{-1}	0.965
F(000)	2668.0
R_1/%	10.11
CCDC number	2524871

Table S7. Photophysical parameters and π-overlap areas of the five crystalline phases.

Crystal	Emission maximum (nm)	Quantum yields (%)	Lifetime (ns)	π-Overlap area (%)
HB-C1	569	2.64	12.70	0
HB-C2	627	9.62	17.82	2.9
BN-C1	680	6.87	2.13	36
BN-C2	715	10.95	7.59	45.5
BN-C3	734	1.21	11.32	64.5