Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information (ESI)

Host-Guest Interaction-Directed Strategy for Managing Mechanochromic Luminescent Behavior by Modulating Molecular Packing and Conformation

Xie Han,*[a,b] DongDong Sun,[a] Shi Tang,[a] Yong Wu,[a] Luyao Wang,[a] Xiongzhi Zhang,[a,b] and Simin Liu*[a,b]

E-mail: hanxie@wust.edu.cn; liusimin@wust.edu.cn

[a] School of Chemistry and Chemical Engineering,Wuhan University of Science and Technology, Wuhan 430081 (P.R. China)

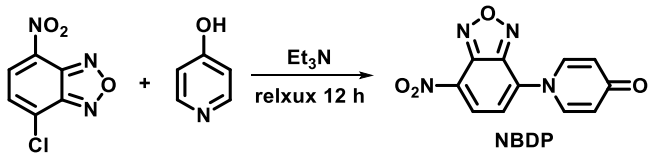
[b] The State Key Laboratory of Refractories and Metallurgy,Wuhan University of Science and Technology, Wuhan 430081 (P.R. China)

Table of Contents

General Information.

CB[8] were prepared by the corresponding literature procedures.[1] Other compounds used in this study were purchased from commercial suppliers and were used without further purification. NMR spectra (^{1}H and ^{13}C) were collected on Agilent 600 MHz DD2 spectrometers. EI-MS was obtained using Thermo scientific DSQⅡ. UV/Vis were performed on a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K. Fluorescence spectra were measured on a PerkinElmer LS-55 machine. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator. PXRD date were collected in a bruker D8 X-ray diffractometer using the Cu Kα line (λ = 1.5418 Å). The quantum chemistry calculation was performed on Gaussian 16 (M06-2X/6-311G(d) basis set) software package. The interaction region plotted by independent gradient model (IGM) was analyzed by means of the Multiwfn package[2] and VMD software.[3]

Synthesis and Characterization：



The synthetic route of **NBDP**

Synthesis of NBDP: 4-chloro-7-nitro-2,1,3-benzoxadiazole (100 mg, 0.5 mmol), 4-Pyridinol (57 mg, 0.6 mmol) and Et_3N (0.1 mL) were dissolved in dry acetonitrile (20 mL) under a nitrogen atmosphere. The reactants were stirred and heated at reflux for 12 h. The mixture was then evaporated and purified by means of column chromatography (DCM：MeOH = 50:1, R_f = 0.15), as a yellow solid (62 mg, 49%).^{1}H NMR (600 MHz, D_2O): δ 8.86(d, *J* = 6 Hz, 1H), 8.48(d, *J* = 12 Hz, 1H),7.99 (d, *J* = 6 Hz, 2H),6.80 (d, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 178.94, 145.48, 143.77, 137.55, 136.51, 130.86, 120.45, 118.83. EI-MS: m/z = 257.95 $[M]^+$; calculated exact mass: 258.04.

Synthesis of NBDP@CB[8]: CB[8] solid (10 mg) was added to the aqueous solution of **NBDP** (1 mM, 1 mL) and followed by ultrasonic treatment for 5 min. The precipitate was centrifuged at 10000 rpm for 2 min and washed with DI water for 3 times, then the separated solid was dried at 60 °C.

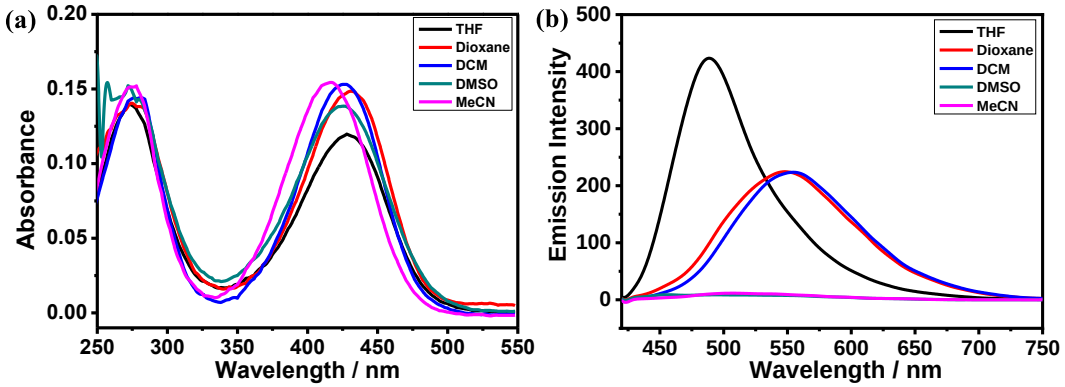


Figure S1. (a) UV/vis absorption and (b) fluorescence spectra of **NBDP** in different solvents (10 uM, λ_{ex} = 420 nm).

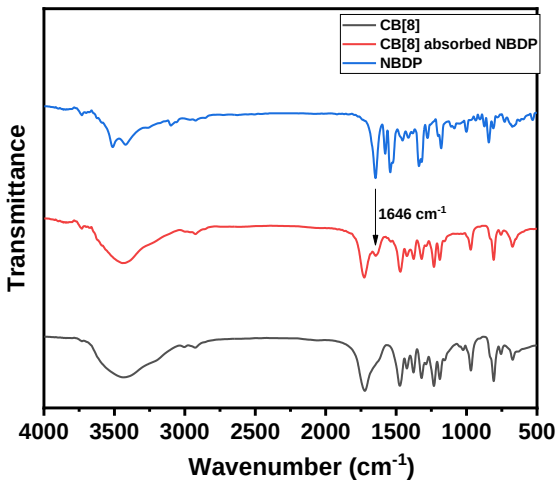


Figure S2 FTIR spectra of CB[8], **NBDP**, and CB[8] that absorbed **NBDP**.

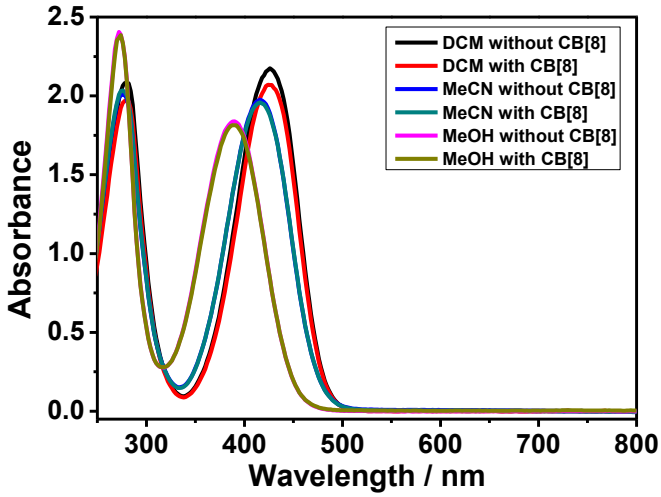


Figure S3 Absorption spectra change of **NBDP** in different solvents in the absence and presence of CB[8].

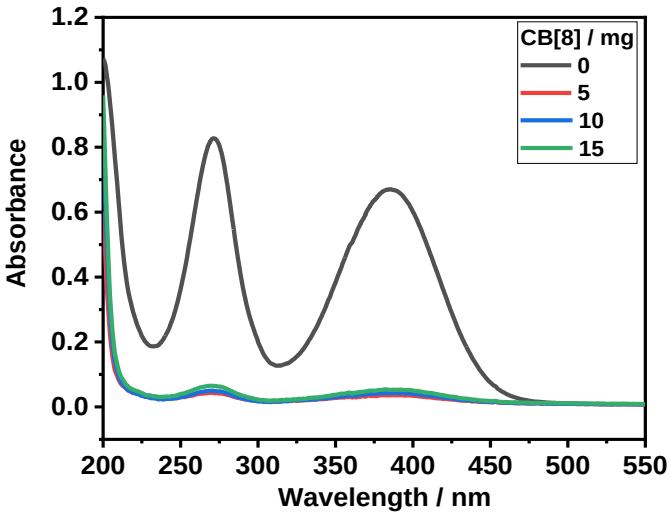


Figure S4 Absorption spectra of **NBDP** aqueous solution (1 mM, 1mL) in the absence and presence of different equivalents of CB[8].

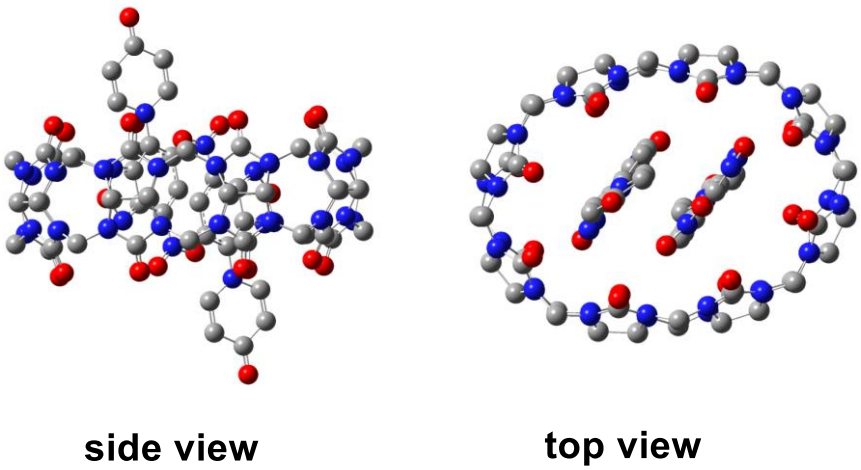


Figure S5. Molecular structures optimized by DFT calculation for **CB[8]·NBDP**$_2$.

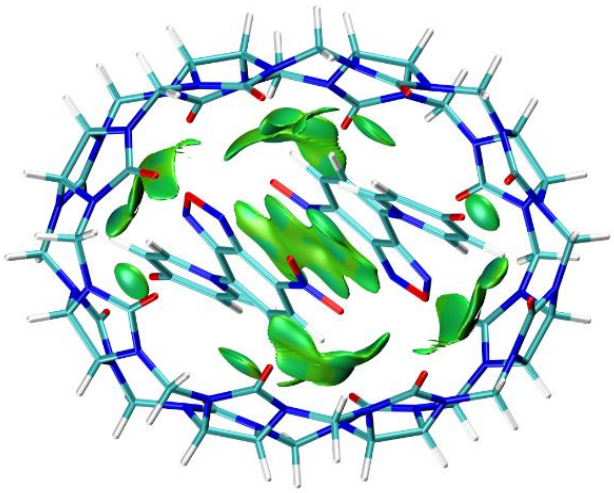


Figure S6 Independent Gradient Model (IGM) analysis of **CB[8]·NBDP**$_2$. Green surfaces represent the van der Waals interaction.

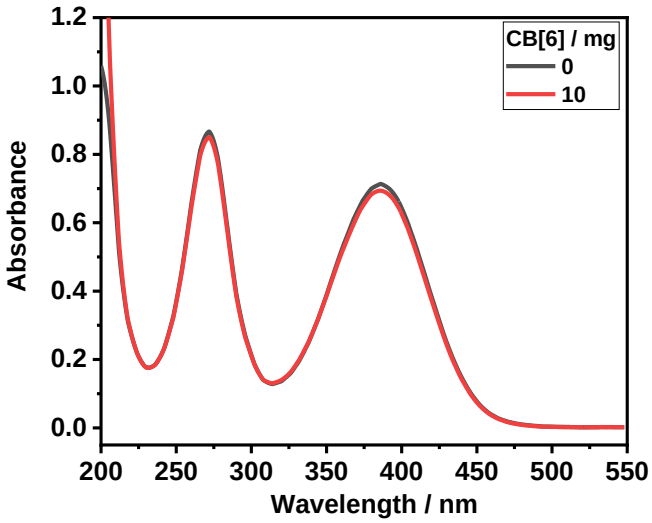


Figure S7 Absorption spectra of **NBDP** aqueous solution (1 mM, 1 mL) in the absence and presence of CB[6].

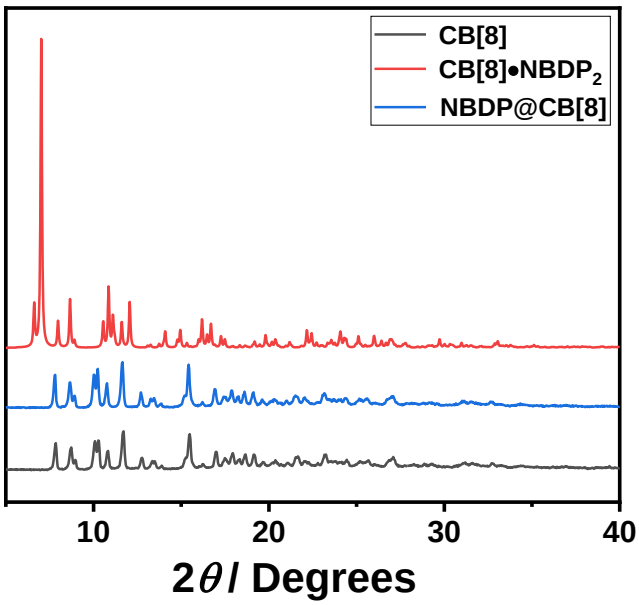


Figure S8 Powder X-ray diffraction (PXRD) patterns of CB[8]**, NBDP@CB[8]** powder and **CB[8]·NBDP$_2$** crystal (simulated from crystal structure of **CB[8]·NBDP$_2$**).

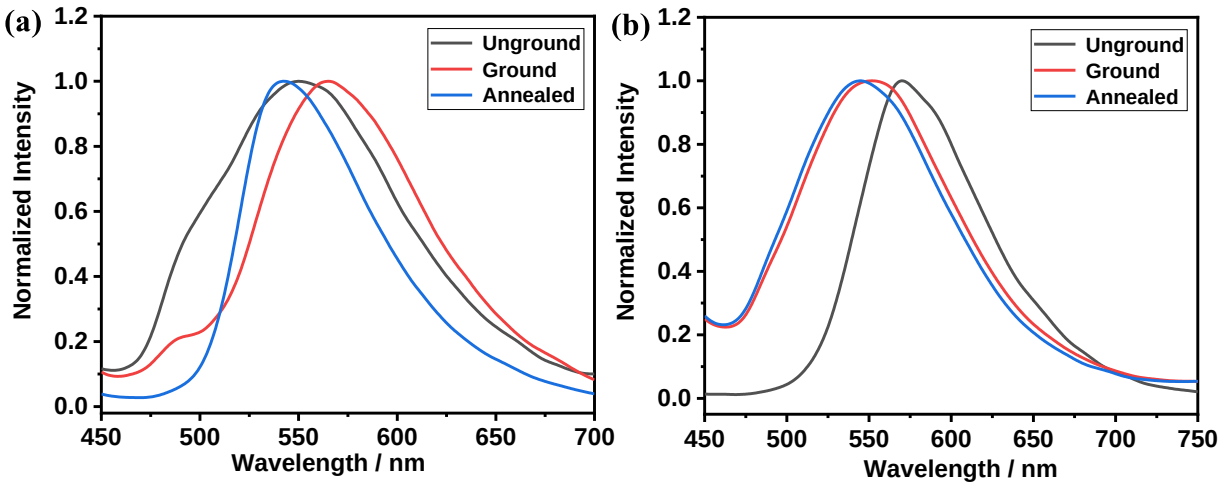


Figure S9 Normalized fluorescence spectra of (a) **NBDP** and (b) **NBDP@CB[8]** powder under different treatments.

Table S1 Fluorescence emission maxima of **NBDP** molecule in its different states.

Compound	λ_{em} (nm) (pristine)[a]	λ_{em} (nm) (ground)	Emission wavelength shift (nm)
NBDP	550	568	18
NBDP-G	534	565	31
NBDP-O	565	565	0
NBDP@CB[8]	569	548	-21[b]
CB[8]·NBDP$_2$	569	579	10

[a]Excited at 400 nm. [b]Blue-shift of the emission after grinding.

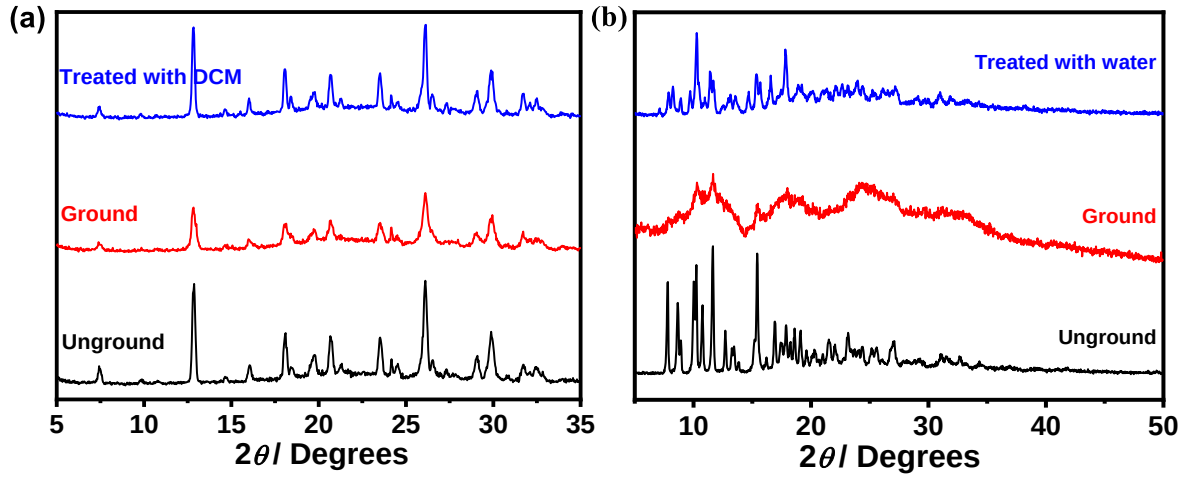


Figure S10 Powder X-ray diffraction (PXRD) patterns of (a) **NBDP** and (b) **NBDP@CB[8]** powder under different treatments.

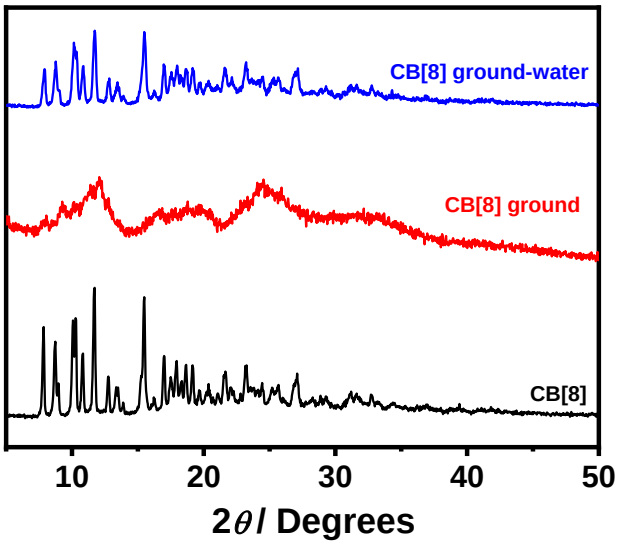


Figure S11 PXRD patterns of CB[8] powder under different treatments.

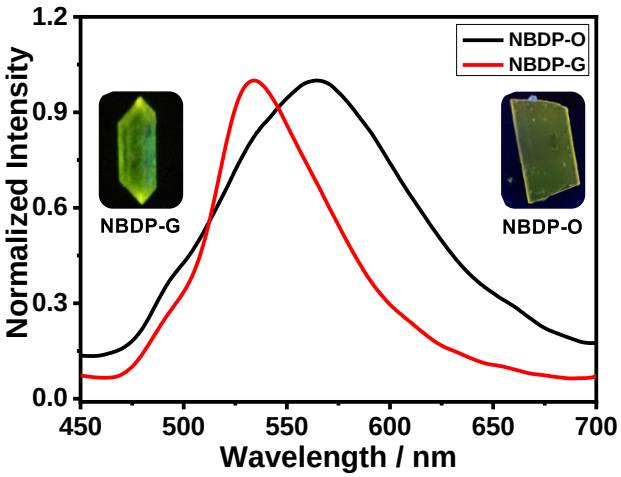


Figure S12 Normalized PL spectra of **NBDP-O** and **NBDP-G**. Insets: Fluorescence images of **NBDP-O** and **NBDP-G** under UV light (365 nm).

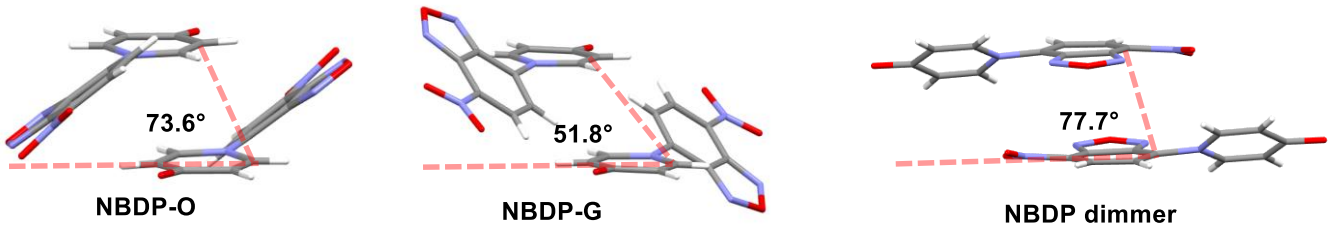


Figure S13 Slip angles of adjacent molecules in **NBDP-O** and **NBDP-G** and **NBDP** dimer in **CB[8]•NBDP$_2$**.

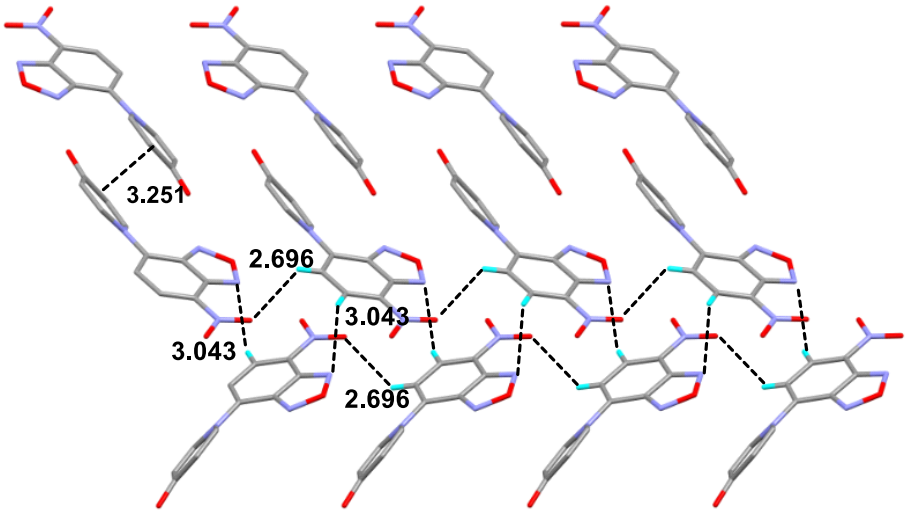


Figure S14 π-π stacking and intermolecular C-H···N, C-H···O interactions in **NBDP-O**.

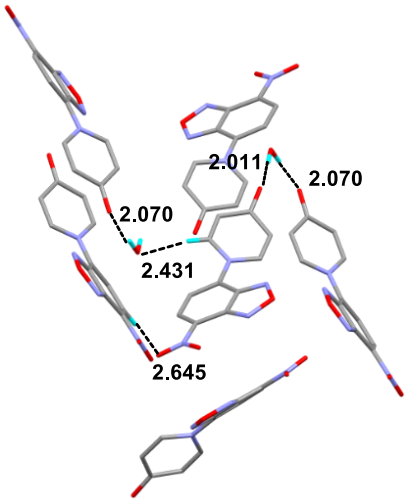


Figure S15 Intermolecular C-H···O and O-H···O interactions in **NBDP-O**.

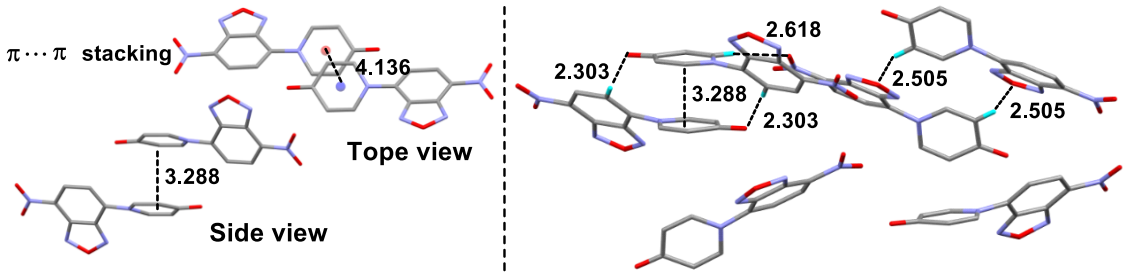


Figure S16 π-π stacking and multiple kinds of intermolecular C-H···O interactions in **NBDP-G**.

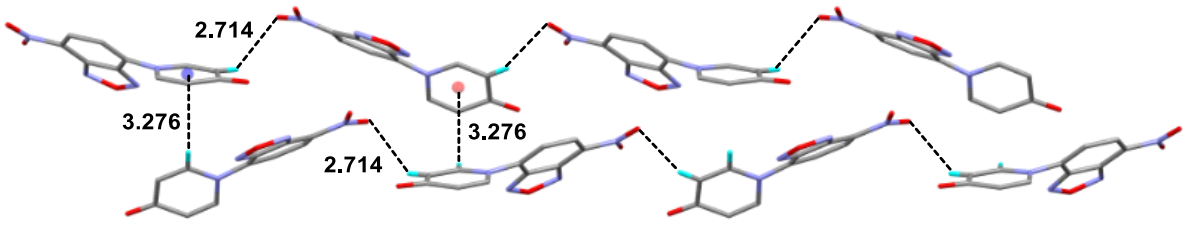


Figure S17 C-H···π and intermolecular C-H···O interactions in **NBDP-G**.

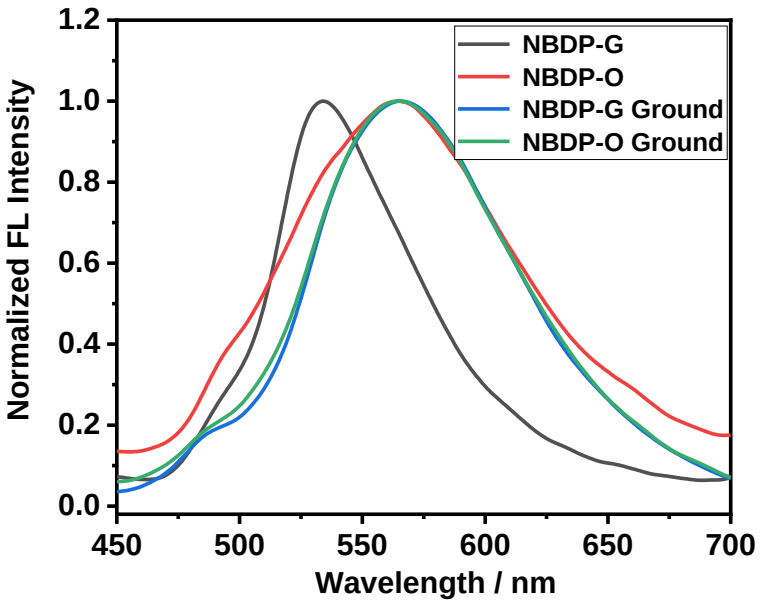


Figure S18 Normalized fluorescence spectra of **NBDP-G and NBDP-O** crystals before and after grinding.

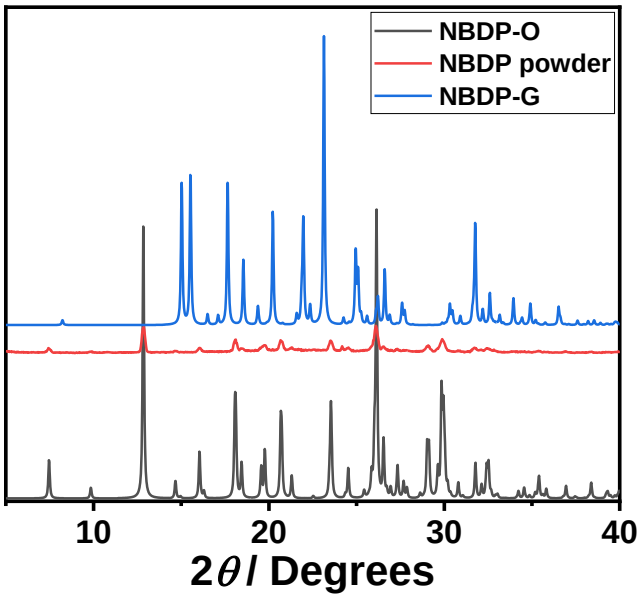


Figure S19 Powder X-ray diffraction (PXRD) patterns of **NBDP** powder, **NBDP-O** and **NBDP-G** crystal (simulated from crystal structure).

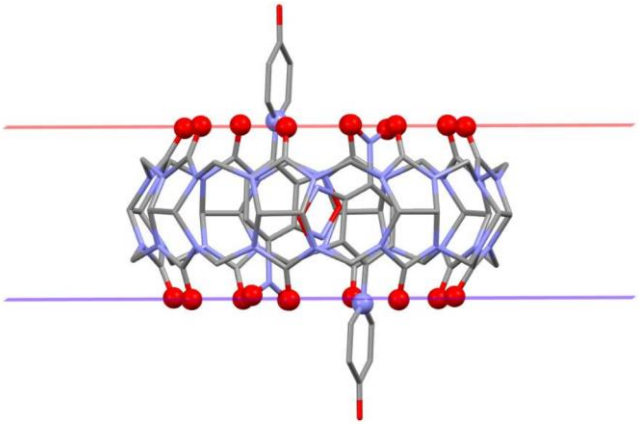


Figure S20 X-ray crystal structure of **CB[8]·NBDP**$_2$.

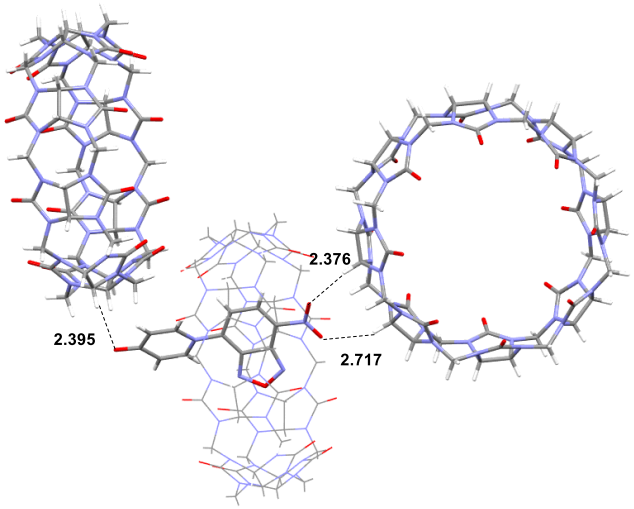


Figure S21 Intermolecular C-H···O interactions between NBDP and CB[8] host of the **CB[8]·NBDP**$_2$ neighbors.

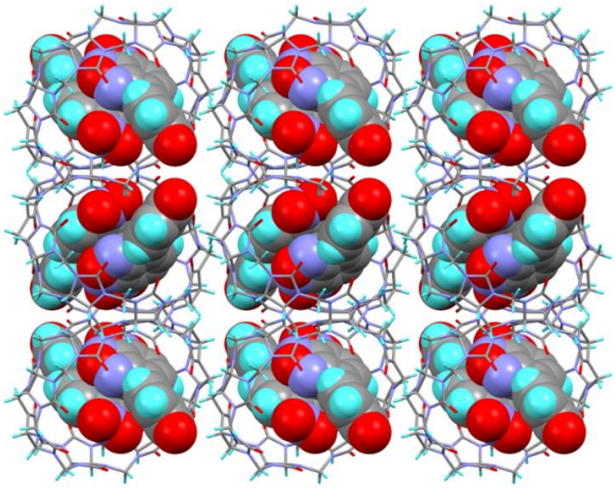


Figure S22 Molecular packing of **CB[8]·NBDP**$_2$ complexes.

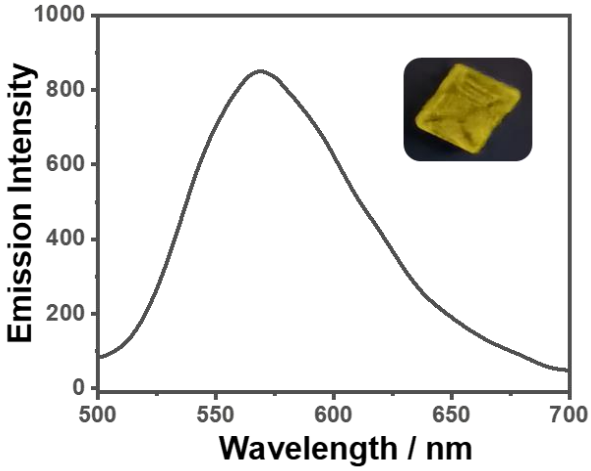


Figure S23 Fluorescence spectra of **CB[8]·NBDP$_2$** crystal. Insets: Fluorescence images of **CB[8]·NBDP$_2$** crystal under UV light (365 nm).

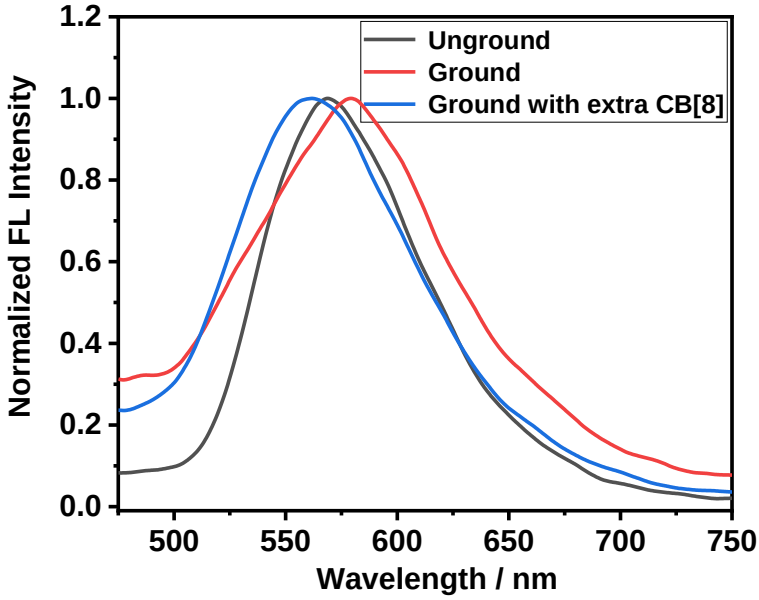


Figure S24 Normalized fluorescence spectra of **CB[8]·NBDP$_2$** crystal under different treatments.

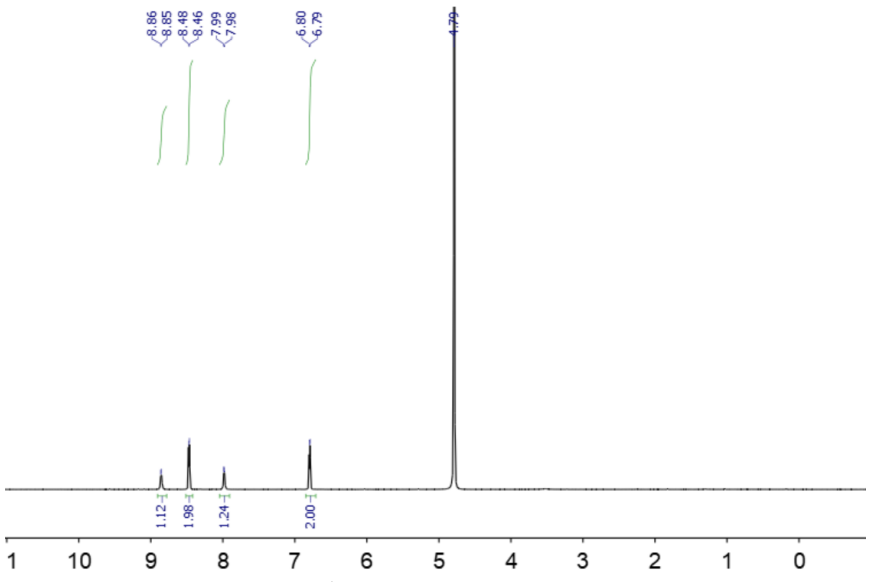


Figure S25 ^{1}H NMR (600 MHz, D_2O) of **NBDP**.

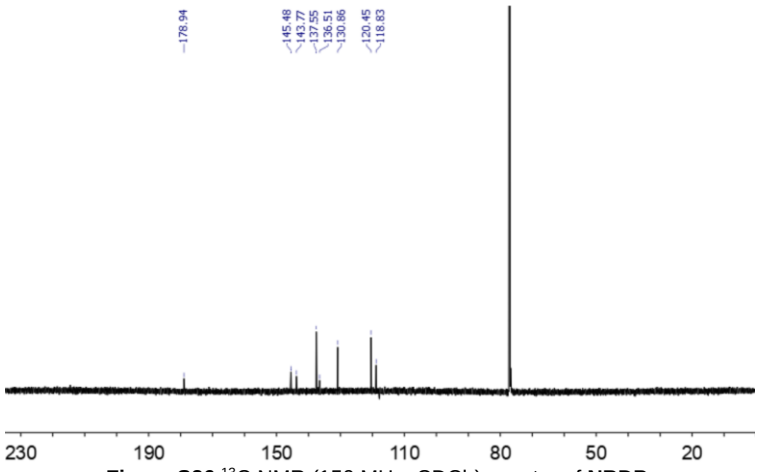


Figure S26 ^{13}C NMR (150 MHz, $CDCl_3$) spectra of **NBDP**.

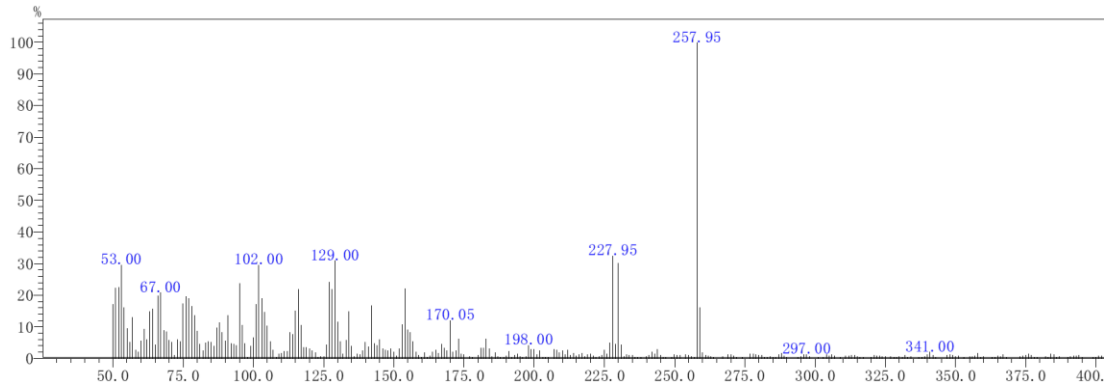


Figure S27 EI/MS spectra of **NBDP**.

Table S2 The main crystallographic parameters of **NBD-O**

Identification code	**NBD-O**
Empirical formula	$C_{11}H_8N_4O_5$
Formula weight	276.21
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.774(2)
b/Å	6.9990(11)
c/Å	23.662(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2281.1(6)
Z	8
ρ_{calc}g/cm^3	1.609
μ/mm^{-1}	0.131
F(000)	1136.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.538 to 60.87
Index ranges	-13 ≤ h ≤ 19, -9 ≤ k ≤ 9, -33 ≤ l ≤ 33
Reflections collected	16732
Independent reflections	3339 [R_{int} = 0.0265, R_{sigma} = 0.0206]
Data/restraints/parameters	3339/0/184
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1368

Final R indexes [all data]	R_1 = 0.0639, wR_2 = 0.1533
Largest diff. peak/hole / e Å^{-3}	0.25/-0.18

Table S3 The main crystallographic parameters of **NBD-G**

Identification code	**NBD-G**
Empirical formula	$C_{11}H_6N_4O_4$
Formula weight	258.20
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.7743(5)
b/Å	11.8277(7)
c/Å	21.4669(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2227.8(2)
Z	8
ρ_{calc}g/cm^3	1.540
μ/mm^{-1}	0.122
F(000)	1056.0
Crystal size/mm^3	0.1 × 0.05 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.794 to 55.194
Index ranges	-6 ≤ h ≤ 11, -15 ≤ k ≤ 13, -19 ≤ l ≤ 26
Reflections collected	9910
Independent reflections	2319 [R_{int} = 0.0245, R_{sigma} = 0.0281]
Data/restraints/parameters	2319/0/173
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.0937
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.1123
Largest diff. peak/hole / e Å^{-3}	0.14/-0.15

Table S4 The main crystallographic parameters of **CB[8]•NBDP$_2$**

compound	**CB[8]•NBDP$_2$**
Empirical formula	$C_{70}H_{60}N_{40}O_{24}$
Formula weight	1845.58
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.794(3)
b/Å	19.827(5)
c/Å	16.822(4)
α/°	90
β/°	104.599(7)
γ/°	90
Volume/Å^3	4452.1(17)
Z	2
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	0.108
F(000)	1904.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.108 to 50
Index ranges	-16 ≤ h ≤ 15, -23 ≤ k ≤ 23, -19 ≤ l ≤ 20

Reflections collected	27742
Independent reflections	7783 [R_{int} = 0.0938, R_{sigma} = 0.0955]
Data/restraints/parameters	7783/0/604
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.1090, wR_2 = 0.2652
Final R indexes [all data]	R_1 = 0.1385, wR_2 = 0.2868
Largest diff. peak/hole / e $Å^{-3}$	0.57/-0.48

References

[1] A. Day, A.P. Arnold, R.J. Blanch and B. Snushall, *J. Org. Chem*. 2001, **66**, 8094–8100
[2] T. Lu and F. Chen, *J. Comput. Chem.* 2012**, 33**, 580-592
[3] W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics Modell.* 1996**, 14**, 33-38