The organic co-crystal formed by naphthalenediimide-based triangular macrocycle and coronene: intermolecular charge transfers and nonlinear optical properties

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†*Electronic supplementary information (ESI) available: The components of the total polarizability α and γ (a.u.) for the studied complexes.*

1. The definitions of Local Orbital Locators (LOL):

Local Orbital Locators (LOL) are bond descriptors based on kinetic energy density used to describe the properties of chemical bonds.

$$LOL(r) = \frac{\tau(r)}{1 + \tau(r)} \tag{1}$$

$$\tau(r) = \frac{D_0(r)}{(1/2)\Sigma \eta_i |\nabla \varphi_i(r)^2} \tag{2}$$

where i, φ was orbital wavefunction and η_i was occupation number of orbital. $D_0(r)$ was energy density.

2. The definitions of reduced density gradient (s):

To distinguish three different types of noncovalent interactions, that are π–π interaction, hydrogen–binding and steric hindrance, the reduced density gradient (s=1/(2(3π2)1/3)|$\nabla\rho$|/ρ4/3) and Sign(λ2)*ρ, as a pair of very important functions for revealing weak interaction region[30], were obtained by Multiwfn_3.8[31].

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \tag{3}$$

Where, ρ was electron density and $\nabla\rho(r)$ was the gradient norm.

3. The definitions of charge density difference (CDD):

The value of CDD can be accurately calculated as:

$$\Delta\rho(r) = \rho^{ele}(r) - \rho^{hole}(r) \tag{4}$$

where $\rho^{ele}(r)$ and $\rho^{hole}(r)$ represents the distribution of electrons and holes respectively. The purple part and the cyan part correspond to the region where electron density increases and decreases after electron excitation respectively.

4. The definitions of a series of indicators:

A series of indicators for the analysis of electron excitation characteristics based on density difference were performed at TD-DFT. The function of overlap between electron and hole distributions can be evaluated as:

$$S_r = \int S_r(r)dr = \int \sqrt{\rho^{hole}(r)\rho^{ele}(r)}dr \tag{5}$$

D index measures the distance between the hole and the electron's center of mass:

$$D_x = |X_{ele} - X_{hole}| \quad D_y = |Y_{ele} - Y_{hole}| \quad D_z = |Z_{ele} - Z_{hole}|$$

$$D = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2} \tag{6}$$

X_{hole} refers to the x-coordinate of the hole's center of mass, which can be obtained by integrating the ρ^{hole} function times the x-coordinate variable in full space. The so-called center of mass corresponds to the most central and representative point of the overall distribution of the function.

Another quantitative description of the distribution characteristics of holes and electrons in total space:

$$\sigma_{hole,x} = \sqrt{\int (x - X_{hole})^2 \rho^{hole}(r)dr}$$

$$\Delta\sigma = |\sigma_{ele}| - |\sigma_{hole}|$$

$$H = (|\sigma_{ele}| - |\sigma_{hole}|)/2$$

$$t = D - H_{CT}$$

$$HDI = 100 \times \sqrt{\int [\rho^{hole}(r)]^2 \, dr}$$

$$EDI = 100 \times \sqrt{\int [\rho^{ele}(r)]^2 \, dr}$$

$$E_c = \iint \frac{\rho^{hole}(r_1)\rho^{ele}(r_2)}{|r_1 - r_2|} \, dr_1 dr_2 \tag{7}$$

The σ index measures the overall distribution of holes, or electrons. Δσ measure the difference in the width of the spatial distribution of electrons and holes. H index reflects the overall average distribution width of electrons and holes. The t index measures the degree of hole and electron separation. t > 0 implies that the separation between the hole and the electron is relatively sufficient due to CT. t< 0 indicates that there is no significant separation between the hole and the electron. The HDI was hole delocalization index, EDI was electron delocalization index and E_c was exciton binding energy.
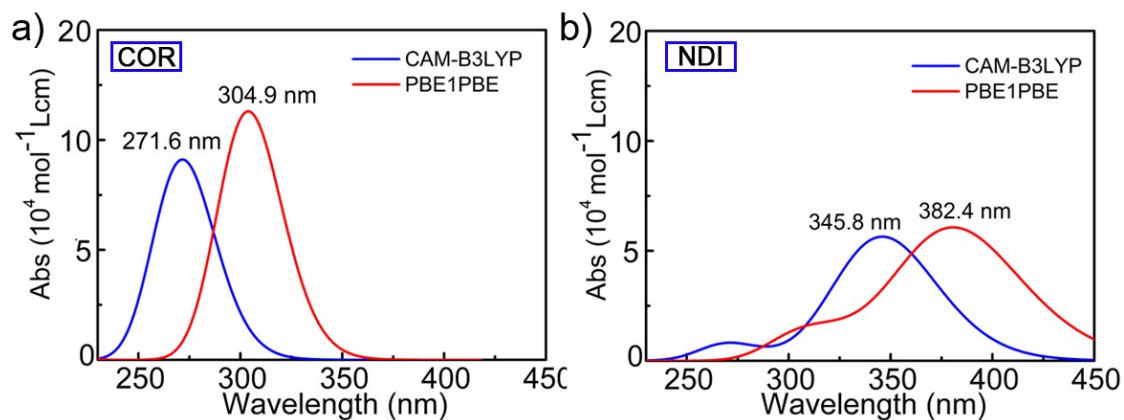
Figure S1. Simulated UV−Vis spectra of COR and NDI at TD-CAM-B3LYP and TD-PBE0 with 6-311+G(d) basis set under the condition of PCM solvent model (solvent=dichloromethane). The spectral envelope was obtained by convolution of the stick spectra using Gaussian function of 0.6 eV FWHM.

Table S1. The maps of natural transition orbital (NTO) and transition density matrix (TDM). The overlap of hole-electron index (Sr, au), the distance between the hole and the electron's center of mass index (D, Å), the overall mean distribution width of electrons and holes index (H, au), hole delocalization index (HDI, au), electron delocalization index (EDI, au), Ghost-hunter index (GHI, eV) of the excited state corresponding to the main absorption peaks.
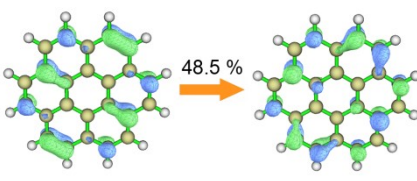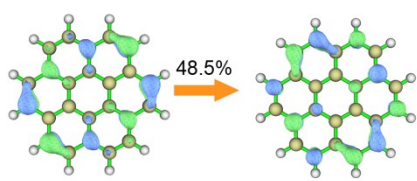
	COR	
State	S_0-S_3	S_0-S_4
	π-π^*	π-π^*
NTO		
TDM		
S_r	0.97 au	0.97 au
D	0.00 Å	0.00 Å
H	3.52 Å	3.53Å
HDI	4.37 au	4.37 au
EDI	4.43 au	4.43 au
GHI	4.54 eV	4.54 eV

Table S2. The maps of natural transition orbital (NTO) and transition density matrix (TDM). The overlap of hole-electron index (Sr, au), the distance between the hole and the electron's center of mass index (D, Å), the overall mean distribution width of electrons and holes index (H, au), hole delocalization index (HDI, au), electron delocalization index (EDI, au), Ghost-hunter index (GHI, eV) of the excited state corresponding to the main absorption peaks.
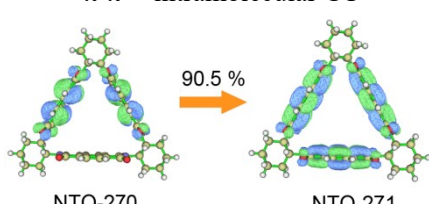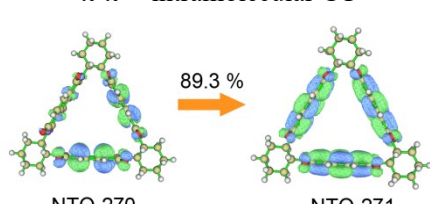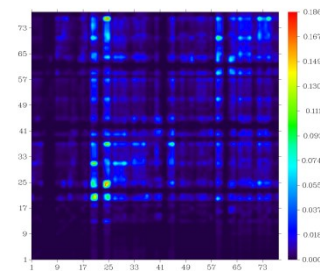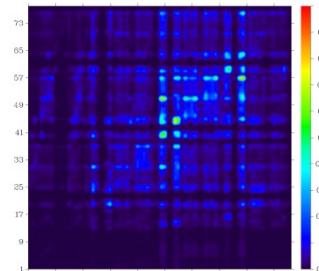
	NDI	
State	S_0-S_2	S_0-S_3
	π-π^*+ intramolecular CT	π-π^*+ intramolecular CT
NTO		
TDM		
S_r	0.79 au	0.82 au
D	1.37 Å	1.24 Å
H	4.71 Å	4.71 Å
HDI	4.59 au	4.96 au
EDI	3.59 au	3.60 au
GHI	3.86 eV	3.87 eV

Table S3. The maps of natural transition orbital (NTO) and transition density matrix (TDM). The overlap of hole-electron index (Sr, au), the distance between the hole and the electron's center of mass index (D, Å), the overall mean distribution width of electrons and holes index (H, au), hole delocalization index (HDI, au), electron delocalization index (EDI, au), Ghost-hunter index (GHI, eV) of the excited state corresponding to the main absorption peaks.
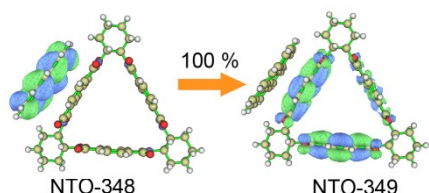
	NDI-COR	
State	S_0-S_2	S_0-S_6
	intermolecular CT	intermolecular CT
NTO		
TDM		
S_r	0.13 au	0.82 au
D	6.94 Å	1.24 Å
H	4.14 Å	4.71 Å
HDI	5.51 au	4.96 au
EDI	4.15 au	3.60 au
GHI	2.42 eV	3.87 eV

Table S4. The maps of natural transition orbital (NTO) and transition density matrix (TDM). The overlap of hole-electron index (Sr, au), the distance between the hole and the electron's center of mass index (D, Å), the overall mean distribution width of electrons and holes index (H, au), hole delocalization index (HDI, au), electron delocalization index (EDI, au), Ghost-hunter index (GHI, eV) of the excited state corresponding to the main absorption peaks.
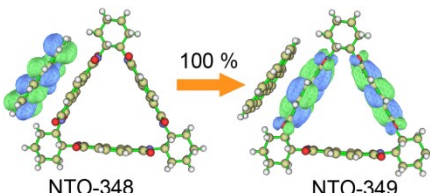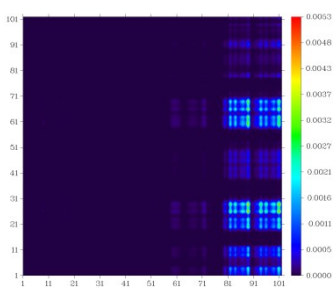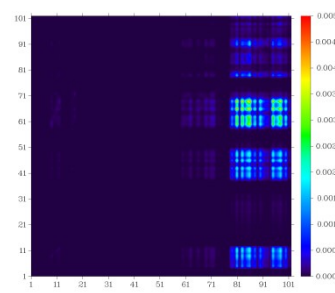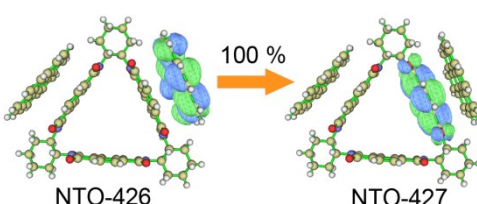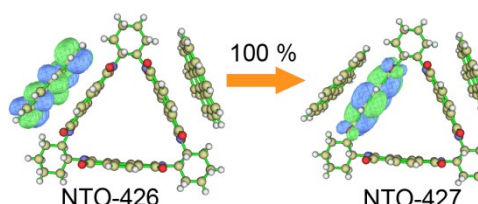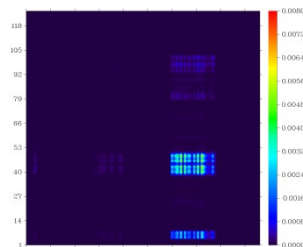
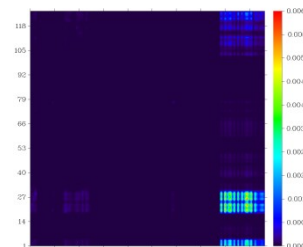|	NDI-COR	NDI-2COR
State	S_0-S_3	S_0-S_4
NTO	Intermolecular CT	Intermolecular CT
TDM		
S_r	1.98 au	0.23 au
D	3.47 Å	3.67 Å
H	3.37 Å	3.46 Å
HDI	5.43 au	5.51 au
EDI	6.26 au	5.86 au
GHI	2.59 eV	2.67 eV

Table S5. The polarizabilities α_{tot} (a.u.) and the components in all directions of the complexes computed at CAM-B3LYP/6-31+G(d) and BHandHLYP/6-311+G(d) level.

Complex	$<R^2>$	Method	α_{xx}	α_{yy}	α_{zz}	α_{tot}
COR	6189.6	CAM-B3LYP	369.2	369.2	115.7	284.7
	6189.1	BHandHLYP	367.8	367.8	115.0	283.5
NDI	65722.4	CAM-B3LYP	748.5	748.6	688.8	728.6
	65725.3	BHandHLYP	758.1	758.3	697.2	737.9
NDI-COR	101456.0	CAM-B3LYP	957.4	893.5	889.2	913.4
	101457.3	BHandHLYP	947.9	883.8	880.7	904.1
NDI-2COR	138230.8	CAM-B3LYP	1147.1	1142.9	1133.1	1141.0
	138231.4	BHandHLYP	1137.6	1133.3	1124.7	1131.8

Table S6. The polarizabilities γ_{tot} (a.u.) and the components in all directions of the complexes computed at CAM-B3LYP/6-31+G(d) and BHandHLYP/6-31+G(d) level.

Complex	Method	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ_{tot}
COR	CAM-B3LYP	136404.0	136407.0	26085.6	45462.3	17689.3	17689.1	92115.6
	BHandHLYP	135717.0	135722.0	26042.6	45233.2	17403.8	26042.6	94968.2
NDI	CAM-B3LYP	290130.0	291573.0	62528.2	95289.8	25836.8	27296.8	188215.6
	BHandHLYP	313894.0	314853.0	65383.4	125706.0	50559.6	48290.7	228648.6
NDI-COR	CAM-B3LYP	264629.0	533524.0	127273.0	125706.0	50559.6	48290.7	274907.7
	BHandHLYP	251658.0	535643.0	126113.0	122080.0	49022.4	46668.1	269791.0
NDI-2COR	CAM-B3LYP	392031.0	709252.0	192790.0	194771.0	66298.8	72068.4	392069.9
	BHandHLYP	391746.0	748950.0	192151.0	203825.0	65230.6	71525.4	402801.8