

Supporting Information

Tuning Optical Properties of π -Conjugated Double Nano hoops under External Electric Field Stimuli-Responsiveness

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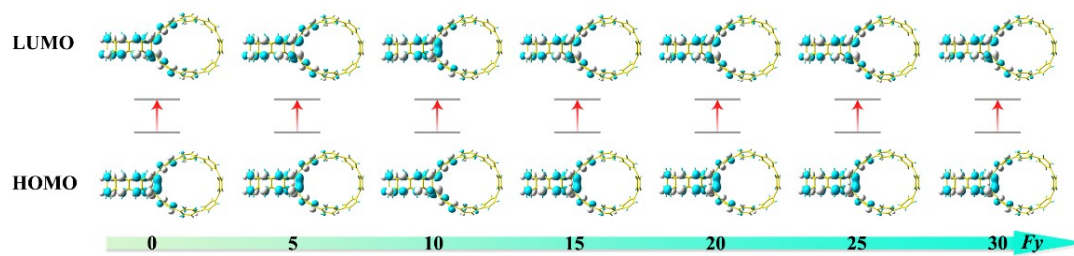


Figure S1. The FMOs of the [8]CPP-[10]cyclacene under the F_y .

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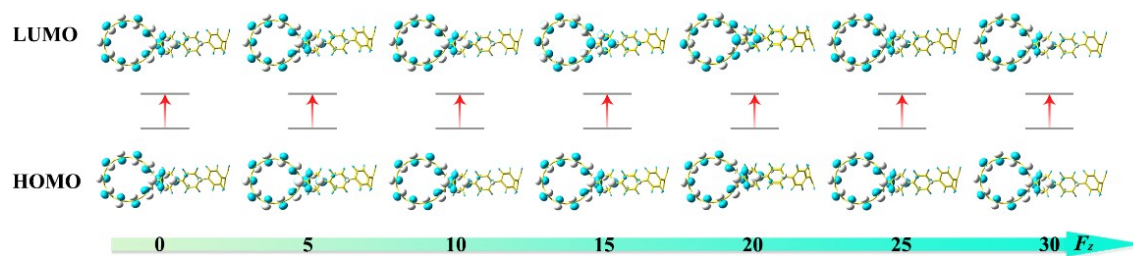


Figure S2. The FMOs of the [8]CPP-[10]cyclacene under the F_z .

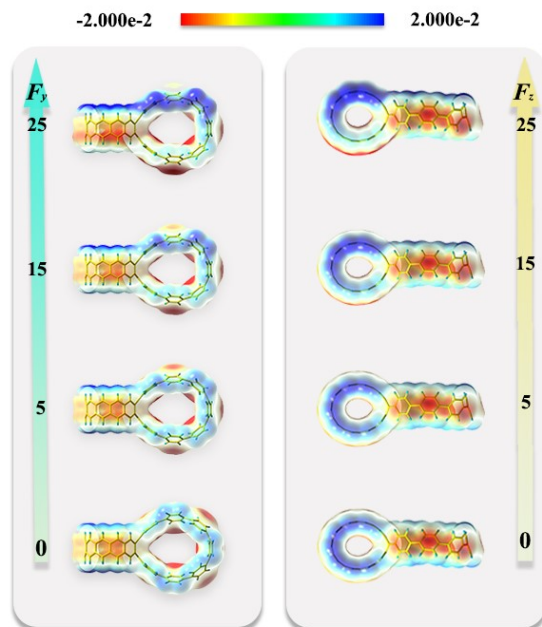


Figure S3. ESP of the [8]CPP-[10]cyclacene under the F_y and F_z .

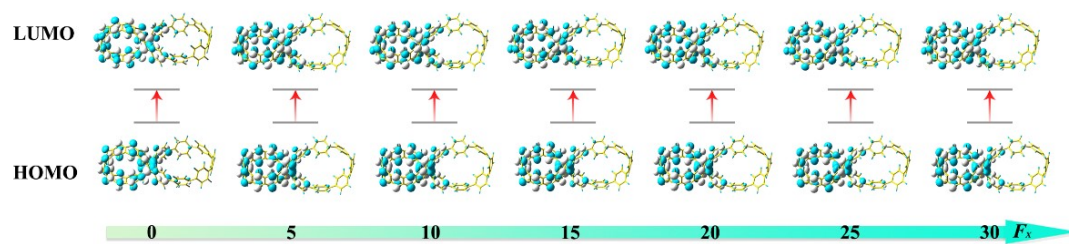


Figure S4. The FMOs of the [8]CPP-[10]cyclacene under the F_x .

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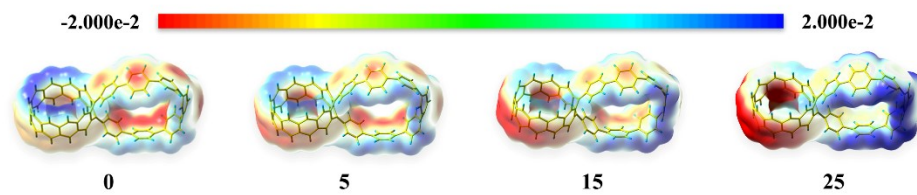


Figure S5. ESP of the [8]CPP-[10]cyclacene under the F_x .

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Table S1. The total energies (E_{UB3LYP} and E_{B3LYP} , au) of the [8]CPP-[10]cyclacene at the B3LYP and UB3LYP level with 6-31G(d) basis set without/ under the horizontal F_y ($F_y = 1 \times 10^{-4}$ au).

$F_y \times 10^{-4}$ (au)	E_{UB3LYP}	E_{B3LYP}
0	-3152.4202	-3152.4024
10	-3152.4206	-3152.4031
20	-3152.4049	-3152.4049
30	-3152.4080	-3152.4080

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Table S2. Diradical characters (y_0 and y_1) for the [8]CPP-[10]cyclacene and [10]C-Ac at the LC-UBLYP/6-31G* level of theory.

Compound	y_0	y_1
[8]CPP-[10]cyclacene	0.936	0.327
[10]C-Ac ¹	0.965	0.336

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The diradical character (y_i), associated with HOMO- i and LUMO+ i , is defined based on the weight of the doubly excited configuration within multiconfigurational (MC)-SCF theory. The y_i is applied within the framework of the spin-unrestricted long-range corrected UBLYP (LC-UBLYP) functional, utilizing the 6-31G(d) basis set.² Meanwhile, the range separating parameter μ of the LC-BLYP functional is set to 0.33 bohr⁻¹. The y_i is formally expressed as follows:^{3, 4}

$$y_i = 1 - 2T_i / (1 + T_i^2) \quad (1)$$

where T_i is the orbital overlap between the corresponding orbital pairs, which can also be expressed as:

$$T_i = (n_{\text{HOMO-}i} - n_{\text{LUMO-}i}) / 2 \quad (2)$$

Table S3. Evolutions of diradical characters (y_0 and y_1) under the F_y .

$F_y \times 10^{-4}$ (au)	y_0	y_1
0	0.94	0.33
5	0.94	0.33
10	0.94	0.33
15	0.94	0.33
20	0.94	0.26
25	0.94	0.26
30	0.94	0.26

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Table S4. Evolutions of diradical characters (y_0 and y_1) under the F_z .

$F_z \times 10^{-4}$ (au)	y_0	y_1
0	0.94	0.33
5	0.94	0.33
10	0.94	0.33
15	0.94	0.33
20	0.94	0.33
25	0.93	0.26
30	0.93	0.26

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Table S5. Evolutions of diradical characters (y_0 and y_1) under the F_z .

$F_x \times 10^{-4}$ (au)	y_0	y_1
0	0.94	0.33
5	0.94	0.26
10	0.93	0.26
15	0.93	0.32
20	0.00	0.00
25	0.59	0.58
30	0.00	0.00

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Table S6. Cartesian coordinates (Å) for the optimized structure by using the UB3LYP-D3 with 6-31G(d) basis set.

Optimized S_0 geometry of the [8]CPP-[10]cyclacene

C	9.03097300	-6.10263200	0.06843800
C	9.61975200	-6.69819700	-1.06595800
H	8.98898800	-7.04105900	-1.88147100
C	11.00181700	-6.79132900	-1.19867100
H	11.42084600	-7.19205200	-2.11816500
C	11.86298500	-6.29974500	-0.19984600
C	11.27046100	-5.88746500	1.00755700
H	11.89792600	-5.50148300	1.80528500
C	9.89121100	-5.78930100	1.13780800
H	9.48987100	-5.33243500	2.03677200
C	14.23024000	-5.78003500	0.55179300
H	14.09093700	-6.32086000	1.48436200
C	13.26444900	-5.89200900	-0.46676400
C	13.55816700	-5.27259100	-1.69421400
H	12.85121800	-5.34865400	-2.51517300
C	14.62488400	-4.38916800	-1.81339600
H	14.71016300	-3.80225500	-2.72273200
C	15.44782800	-4.08916000	-0.71234000
C	15.30262800	-4.90146500	0.42945500
H	15.98014300	-4.77487600	1.26985600
C	15.98728000	-0.62309900	0.50853900
H	15.72459500	-0.09802900	1.42165400
C	16.08699400	0.08904800	-0.70037200
C	16.46022600	-0.64903200	-1.84078500
H	16.65121800	-0.13226800	-2.77778000
C	16.46509800	-2.04121400	-1.82355600
H	16.65970300	-2.57962800	-2.74751800
C	16.09672000	-2.75338500	-0.66522800
C	15.99201400	-2.01221900	0.52568600
H	15.73276200	-2.51646700	1.45141600
C	15.42891700	1.41872600	-0.78043400
C	14.60298700	1.68519300	-1.88784700
H	14.69151400	1.07602500	-2.78211800
C	13.53032700	2.56403000	-1.78991800
H	12.82211700	2.61450200	-2.61175400
C	13.23349700	3.21230600	-0.57821700
C	14.20091500	3.13267700	0.44181100
H	14.05884400	3.69601900	1.36053200
C	15.27919900	2.25862200	0.34060600
H	15.95840000	2.15795300	1.18312400
C	11.82949200	3.61711300	-0.32019400
C	10.96452900	4.07898700	-1.32984900
H	11.38038600	4.46024400	-2.25901600
C	9.58318300	3.98022800	-1.19374000
H	8.94957200	4.29925400	-2.01670200
C	8.99903700	3.40816600	-0.04491600
C	9.86198200	3.12586500	1.03086400
H	9.46418600	2.68786800	1.94071900
C	11.24048200	3.22984900	0.89715300

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H	11.87099200	2.86701000	1.70327300
C	7.61688500	2.88096100	-0.03133400
C	7.03399700	2.39853800	-1.22269100
H	7.52697500	2.58262400	-2.17237800
C	5.92402500	1.57245200	-1.20837500
H	5.58437400	1.14219200	-2.14381800
C	5.31985600	1.15708600	0.00994600
C	5.82855800	1.75557000	1.19582000
H	5.40023600	1.49022800	2.15572200
C	6.93061800	2.59358100	1.16869200
H	7.30445800	2.99164000	2.10791900
C	4.42638700	0.03141000	0.03821200
C	3.90675700	-0.64920400	-1.14390500
C	3.91199900	-2.10533400	-1.12731900
C	4.43613800	-2.75489600	0.07015300
C	5.33710700	-3.87496900	0.06832900
C	5.84906200	-4.44201800	1.26817100
C	5.94471000	-4.31492700	-1.13959900
C	6.95657600	-5.27315500	1.26130500
H	5.41851000	-4.15705000	2.22141700
C	7.06010600	-5.13385500	-1.13394100
H	5.60281300	-3.90903000	-2.08506800
C	7.64545600	-5.58423200	0.06871000
H	7.33240900	-5.64653400	2.20982400
H	7.55477600	-5.33707500	-2.07884200
C	3.90663700	-2.07990800	1.25209800
C	3.19770200	-2.74838900	2.23944900
C	2.24620600	-2.06057800	3.04448200
C	2.24089700	-0.60984400	3.02775700
C	3.18763100	0.06609700	2.20717600
C	3.90148600	-0.61983300	1.23543700
C	1.13931000	-2.74087900	3.57375000
C	1.12898500	0.07436200	3.54125400
H	1.13439400	-3.82877100	3.55357000
H	3.16294400	-3.83435100	2.22170900
H	3.14520800	1.15109800	2.16445200
H	1.11621200	1.16144900	3.49628900
C	-0.08135600	-2.06337800	3.78230600
C	-0.08670300	-0.60707600	3.76556300
C	-1.31812200	0.06825400	3.62814500
H	-1.31360700	1.15543400	3.58697600
C	-1.30772800	-2.75076200	3.66043000
H	-1.29510200	-3.83853200	3.64401600
C	3.21365000	-2.79827500	-2.10571100
C	2.26534100	-2.12931800	-2.92964800
C	2.26014100	-0.67798100	-2.94614500
C	3.20360000	0.01628900	-2.13772500
C	1.16179200	-2.82148200	-3.45058700
C	1.15169600	-0.00574400	-3.48253900
C	-0.06273200	-0.69230400	-3.69804700
C	-0.05749600	-2.14871900	-3.68156200
C	-1.28469000	-2.83304500	-3.55155400
H	-1.27245800	-3.92017000	-3.51055400

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C	-1.29482000	-0.01403900	-3.58347300
H	1.15693500	-3.90864100	-3.40643500
H	3.19223100	-3.88436100	-2.07009400
H	3.17453700	1.10273000	-2.12694200
H	1.13896700	1.08206900	-3.46287400
H	-1.29031800	1.07379300	-3.56687300
C	-2.43718100	-2.08066700	3.15380000
C	-3.36592900	-2.77440200	2.34506800
C	-3.95905700	-2.10878800	1.25429200
C	-3.96447500	-0.64817500	1.23769700
C	-3.37650100	0.04654600	2.31296900
C	-2.44259900	-0.62159600	3.13719600
C	-4.17881600	-2.80399200	0.04536300
C	-4.18924900	0.01770100	0.01328400
C	-3.95668300	-0.67580900	-1.19412200
C	-3.95132400	-2.13643700	-1.17754500
C	-3.35125200	-2.82668700	-2.24913700
H	-3.32626400	-3.91393700	-2.22043400
C	-2.41725000	-2.15156800	-3.06737000
C	-2.42251400	-0.69248800	-3.08389400
C	-3.36144100	-0.00574100	-2.28113200
H	-4.14930200	-3.89139200	0.05783600
H	-3.34065100	-3.86201600	2.34121700
H	-3.35943800	1.13395100	2.28433900
H	-4.16770500	1.10529100	0.00099800
H	-3.34433700	1.08203400	-2.27711200

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