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1,4-azaborine as controller of triplet energy, exciton distribution, and aromaticity in [6]cycloparaphenylenes

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Tables and figures

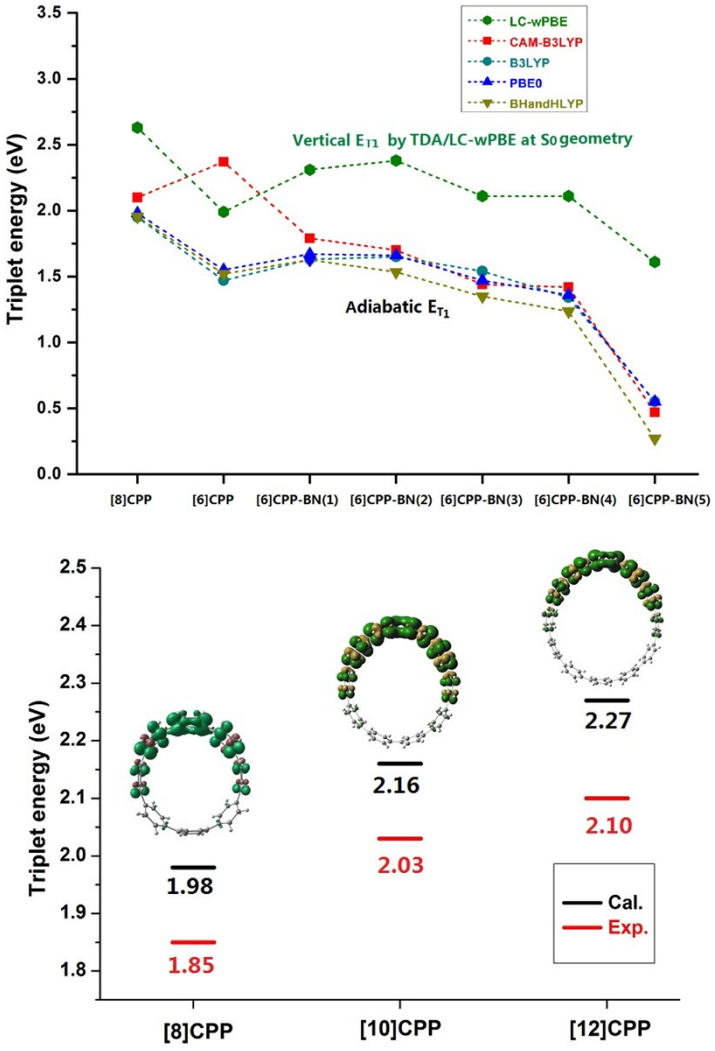


Fig. S1. a. The calculated adiabatic T_1 energies for mono-BN substituted [6]CPP systems, [6]CPP, and [8]CPP by means of the ΔSCF method on the basis of the optimized structures for T_1 and S_0 states. The stable geometries of S_0 and T_1 states were optimized via DFT and unrestricted DFT methods with a varying fraction of HF exchange, respectively. The vertical T_1 energies for seven systems are based on TDA/LC-ωPBE calculation at the S_0 states. **b.** Spin density distribution, the calculated and experimental T_1 energies for [n]CPP (n = 8, 10, 12).

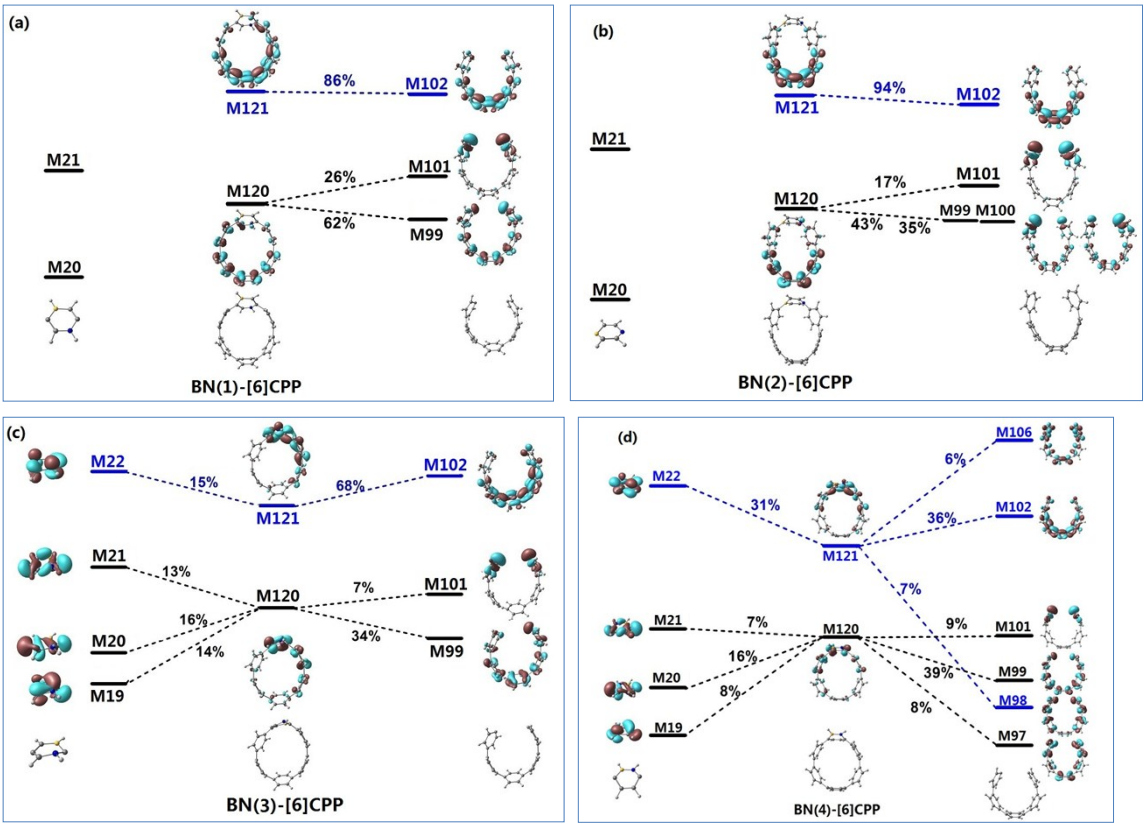


Fig. S2. Molecular orbital correlation diagram for the five isomeric mono-BN [6]CPP systems.

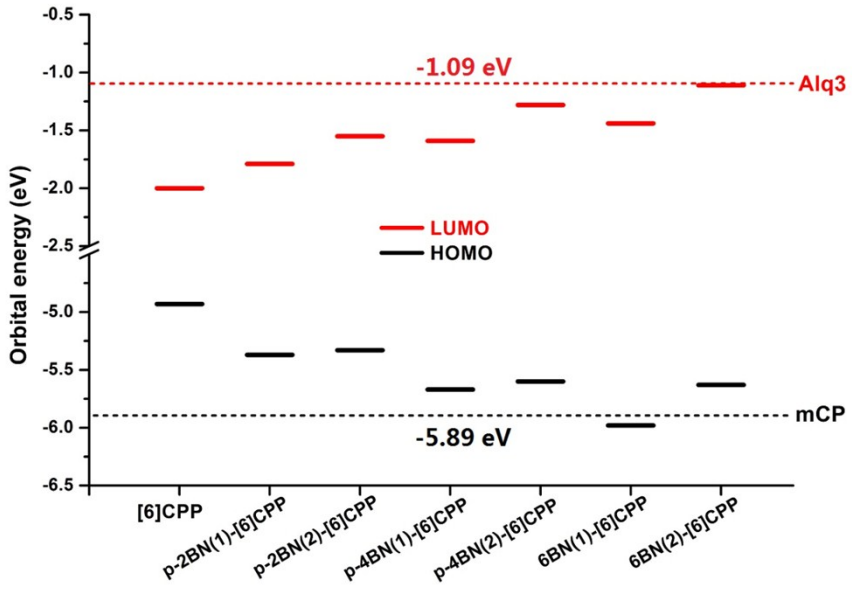


Fig. S3. Energies of HOMOs and LUMOs for [6]CPP and *p*-(n)BN-[6]CPPs in the ground states correspond to the HOMO and LUMO energies of *m*CP and Alq3, respectively.

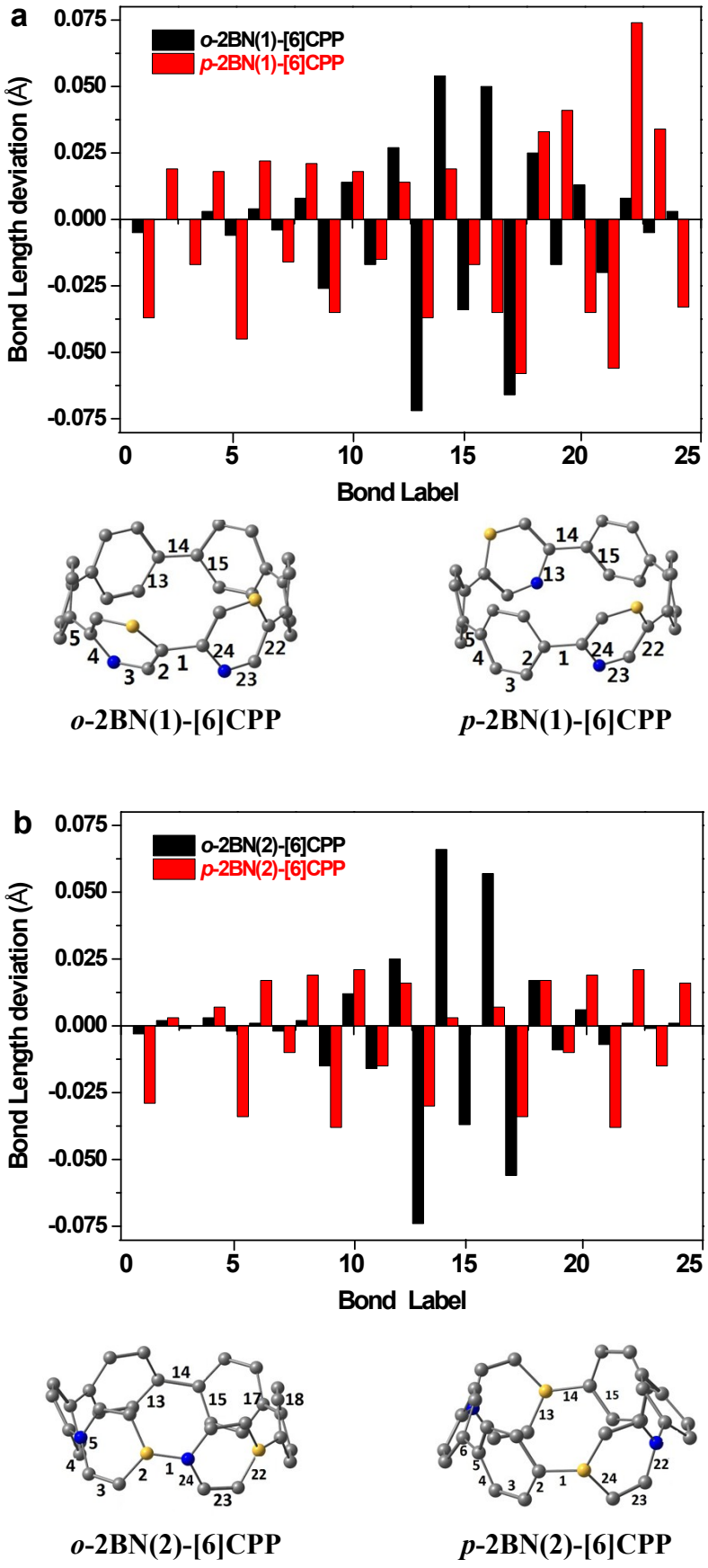


Fig. S4. Bond length deviations between S_0 and T_1 geometries for *o*-2BN(2)-[6]CPP and *p*-2BN(2)-

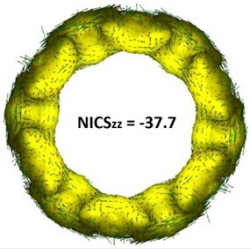
[6]CPP. Atomic label are shown in Fig. S1.

Tables

Table S1 Triplet transition contribution at TDA/LC-ωPBE/6-31G* level at the optimized T_1-state geometries.

Compounds	ω	Triplet transition nature (main contribution)
[8]CPP	0.392	M160→M161 (74.20%)
[6]CPP	0.211	M120→M121 (77.40%)
[6]CPP-BN(1)	0.194	M120→M121 (83.72%)
[6]CPP-BN(2)	0.202	M120→M121 (85.73%)
[6]CPP-BN(3)	0.203	M120→M121 (92.71%)
[6]CPP-BN(4)	0.197	M120→M121 (84.74%)
[6]CPP-BN(5)	0.171	M120→M121 (91.91%)

Table S2 $NICS(1)_{ZZ}$ values (Units in ppm) and total induced current density plots for BN-substituted [6]CPPs.

<table>
<tr><td colspan="3">The NICS(1)zz values at the S_0 geometry</td></tr>
<tr><td>[6]CPP</td><td>p-2BN(2)-[6]CPP</td><td>p-4BN(2)-[6]CPP</td></tr>
<tr><td>10.5</td><td>2.82</td><td>5.14</td></tr>
<tr><td colspan="3">At the T_1 geometry</td></tr>
<tr><td colspan="3">[6]CPP
 
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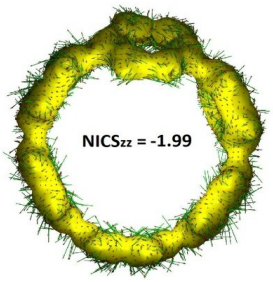
<tr><td colspan="2">o-2BN(1)-[6]CPP
 
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 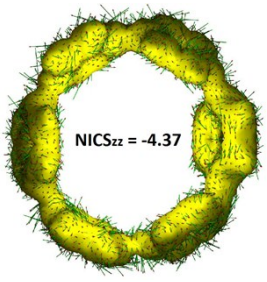
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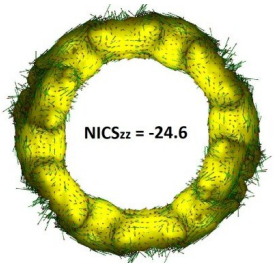
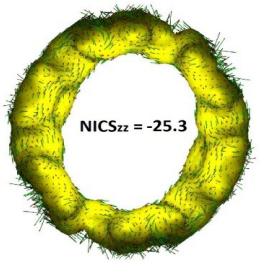
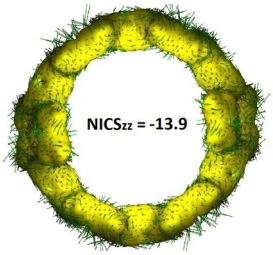
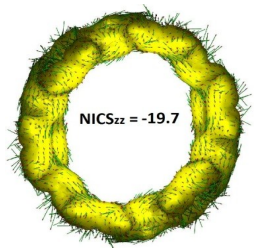
</table>

p-2BN(1)-[6]CPP	*p*-2BN(2)-[6]CPP
	
***p*-4BN(1)-[6]CPP**	***p*-4BN(2)-[6]CPP**
	
6NB(1)-[6]CPP	**6NB(2)-[6]CPP**