Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Effect of Curvature and Placement of Donor and Acceptor Units in Cycloparaphenylenes: A Computational Study.

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1. Calculation Input Files

a) Geometry Optimization

#n CAM-B3LYP/6-311G** Opt Freq scrf=(solvent=dichloromethane)

b) UV-Vis

#n CAM-B3LYP/6-311G** TD=NSTATE=12 scrf=(solvent=dichloromethane)

c) Excited-State Geometry Optimization

#n CAM-B3LYP/6-311G** Opt TD scrf=(solvent=dichloromethane)

d) Fluorescence

#n CAM-B3LYP/6-311G** TD=NSTATE=12 scrf=(solvent=dichloromethane)

2. Electron Accepting and Donating Units Analyzed

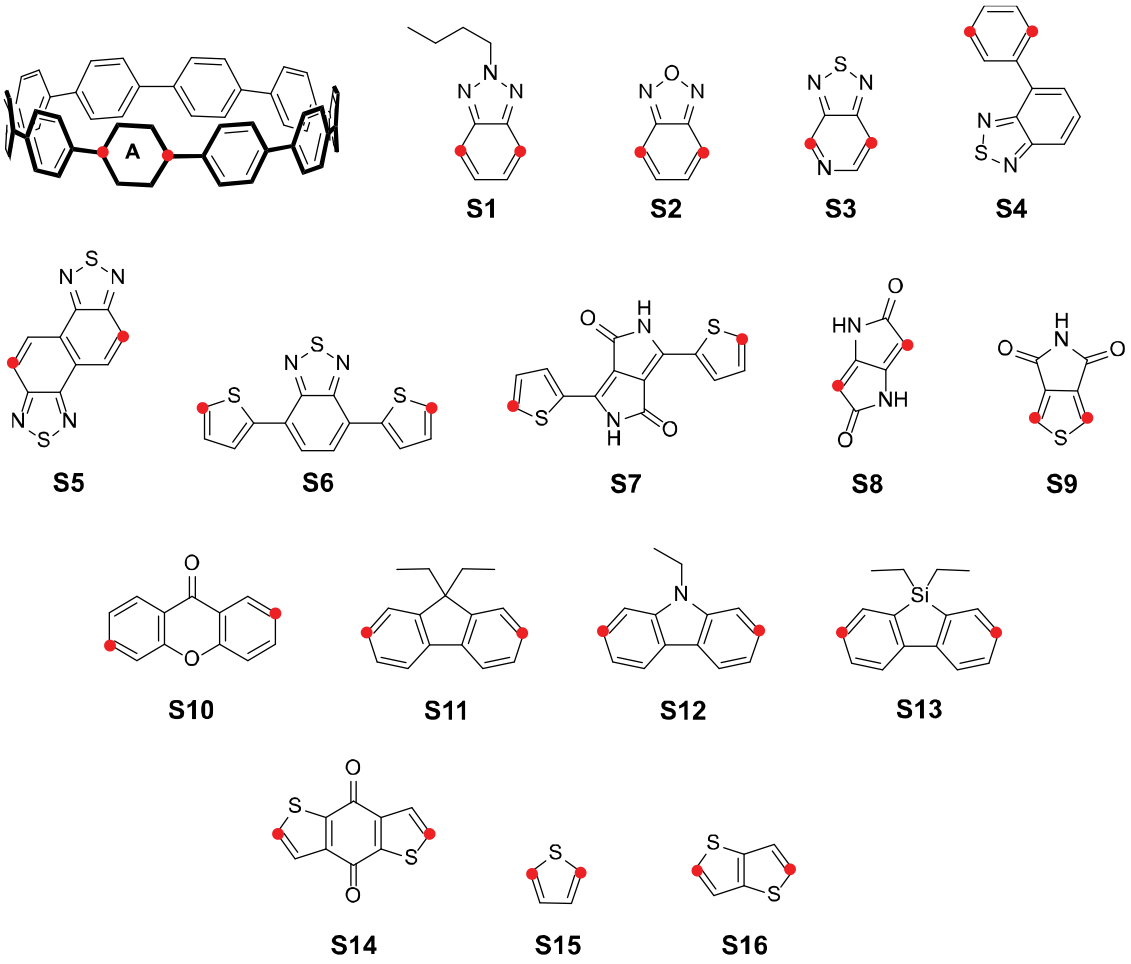


Figure S1. Various electron accepting and donating units on [10]CPP. Note that **S6** replaces three phenylene rings in the [10]CPP, rather than one.

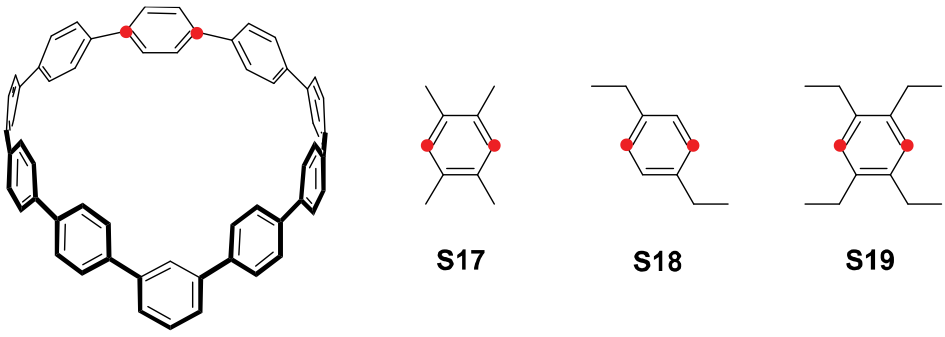
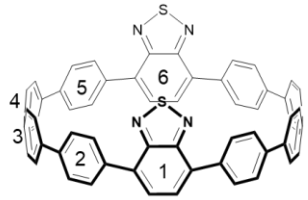
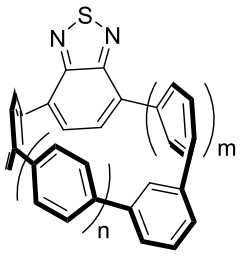


Figure S2. Various dihedral compounds.



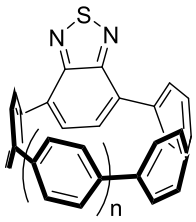
S20. 1,2 positions
S21. 1,3 positions
S22. 1,4 positions
S23. 1,5 positions
S24. 1,6 positions

Figure S3. Multiple BTD units in [10]CPP with varying relative positions.



S25. n = 1, m = 1
S26. n = 2, m = 2
S27. n = 3, m = 3

Figure S4. BTD*m*[*n*]CPP compounds.



S28. n = 1
S29. n = 2
S30. n = 3
S31. n = 4
S32. n = 5

Figure S5. BTD[*n*]CPP compounds.

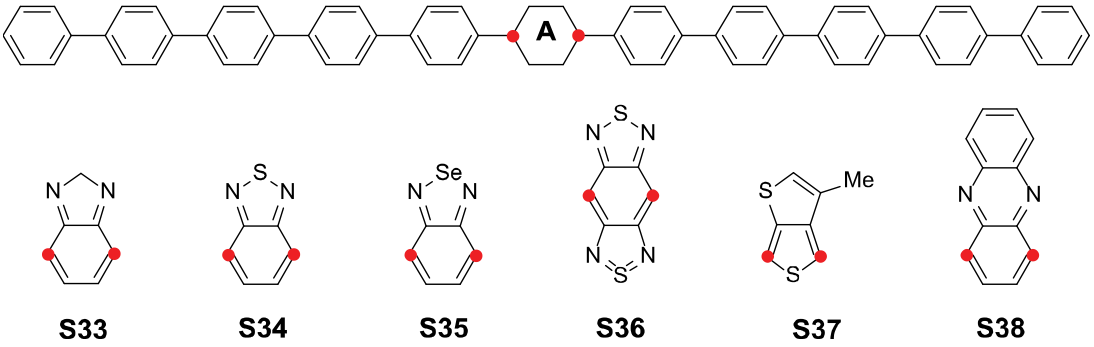


Figure S6. Linear systems with various acceptor units.

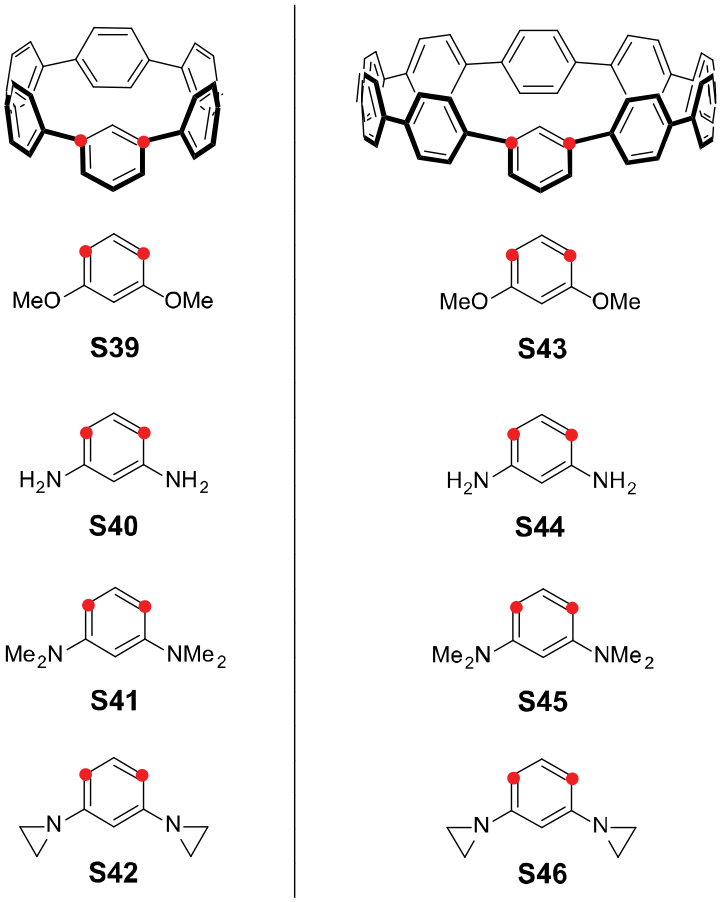


Figure S7. Electron donating groups on *meta*-connected phenylene of *m*[6]CPP and *m*[10]CPP.

3. Absorbance Information of Calculated Compounds

Table S1: Calculated Absorbance of Various Acceptors and Donors on [10]CPP

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
[10]CPP	355	0.049	HOMO → LUMO (67%), H-1 → L+1 (16%), H-2 → L+2 (12%),
	314	2.2077	H-1 → LUMO (44%), HOMO → L+1 (43%)
BT[10]CPP	396	0.4924	HOMO → LUMO (54%), H-1 → LUMO (35%)
	310	2.0711	H-2 → LUMO (37%), HOMO → L+2 (25%), H-2 → L+1 (16%)
1	406	0.2985	H-2 → LUMO (45%), HOMO → LUMO (31%), H-4 → LUMO (13%)
	311	1.9291	H-1 → L+2 (38%), HOMO → L+3 (26%), HOMO → L+1 (14%)
2	656	0.3838	HOMO → LUMO (81%), H-1 → LUMO (17%)
	301	1.346	H-1 → L+1 (26%), HOMO → L+4 (38%)
3	417	0.396	HOMO → LUMO (52%), H-1 → LUMO (36%)
	317	1.714	H-2 → LUMO (38%), HOMO → L+2 (18%), H-2 → L+1 (11%)
4	448	0.4722	HOMO → LUMO (49%), H-1 → LUMO (39%)
	324	1.139	H-2 → LUMO (49%), H-4 → LUMO (11%), HOMO → L+2 (10%)
5	410	0.2927	H-2 → LUMO (42%), HOMO → LUMO (39%)
	288	1.4445	H-2 → L+1 (27%), HOMO → L+3 (31%)
6	350	0.048	H-1 → L+1 (13%), HOMO → LUMO (47%), HOMO → L+1 (11%)
	308	2.6904	H-2 → LUMO (34%), HOMO → L+2 (31%)
S1	371	0.5375	HOMO → LUMO (69%),

			H-1 → LUMO (11%)
	310	2.4275	HOMO → L+2 (34%), H-2 → LUMO (33%)
S2	413	0.6045	HOMO → LUMO (48%), H-1 → LUMO (40%)
	317	1.6571	H-2 → LUMO (46%), HOMO → L+2 (18%), H-3 → LUMO (11%)
S3	436	0.5668	HOMO → LUMO (47%), H-1 → LUMO (41%)
	292	1.3795	H-2 → L+1 (25%), HOMO → L+2 (29%)
S4	312	0.663	H-2 → LUMO (31%), HOMO → LUMO (26%), H-2 → LUMO (10%)
	307	1.8207	H-1 → L+1 (29%), HOMO → L+2 (28%), H-2 → LUMO (10%)
S5	336	0.8996	H-3 → LUMO (26%), H-1 → L+1 (11%), HOMO → LUMO (30%)
	295	1.1721	H-2 → LUMO (20%), HOMO → L+3 (13%)
S6	435	0.5037	H-1 → LUMO (29%), HOMO → LUMO (63%)
	296	1.231	H-2 → L+1 (12%), H-1 → L+1 (15%), HOMO → L+2 (11%), HOMO → L+3 (29%)
S7	498	0.9093	HOMO → LUMO (90%)
	354	1.5791	H-4 → LUMO (12%), H-2 → LUMO (23%), H-1 → LUMO (10%), HOMO → L+1 (22%)
S8	383	0.6971	H-2 → LUMO (44%), HOMO → LUMO (41%)
	304	2.2463	H-1 → LUMO (14%), H-1 → L+1 (20%), HOMO → L+2 (32%)
S9	650	0.1631	H-2 → LUMO (21%), HOMO → LUMO (35%)
	325	1.908	H-2 → L+1 (13%), H-1 → LUMO (17%), HOMO → L+1 (28%),

			HOMO → L+2 (11%)
S10	335	0.2925	H-1 → L+2 (12%), HOMO → LUMO (15%), HOMO → L+1 (39%)
	313	2.6238	H-2 → LUMO (12%), H-1 → LUMO (14%), HOMO → L+1 (19%)
S11	332	0.061	H-2 → L+2 (17%), H-1 → L+1 (19%), HOMO → LUMO (51%)
	303	2.8266	H-2 → L+2 (17%), H-1 → L+1 (19%), HOMO → LUMO (51%)
S12	341	0.001	H-1 → L+1 (10%), HOMO → LUMO (51%)
	316	2.6138	H-1 → LUMO (32%), HOMO → L+1 (36%)
S13	337	0.2398	H-2 → L+2 (13%), H-1 → L+1 (17%), HOMO → LUMO (56%)
	304	2.8218	H-2 → LUMO (38%), HOMO → L+2 (36%)
S14	448	0.1209	H-4 → LUMO (18%), H-2 → LUMO (48%), HOMO → LUMO (23%)
	301	1.7071	H-2 → L+1 (33%), HOMO → L+3 (29%)
S15	341	0.1447	H-2 → L+1 (14%), H-1 → L+2 (15%), HOMO → LUMO (61%)
	306	2.5679	H-2 → LUMO (39%), HOMO → L+1 (39%)
S16	363	0.7022	HOMO → LUMO (78%)
	310	2.4411	H-3 → LUMO (12%), H-2 → L+1 (10%), H-1 → LUMO (20%), HOMO → L+1 (25%)

Table S2: Calculated Absorbance of diBT[10]CPP Compounds

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
S20	410	0.5842	H-2 → LUMO (19%), H-1 → LUMO (15%), HOMO → LUMO (50%)
	294	1.2522	H-3 → LUMO (12%), H-1 → L+2 (19%), HOMO → L+3 (28%)
S21	423	0.5664	H-1 → LUMO (15%), HOMO → LUMO (64%)
	323	0.9985	H-2 → L+3 (10%), H-1 → LUMO (12%), H-1 → L+2 (17%), HOMO → L+2 (35%)
S22	416	0.3427	H-1 → L+1 (20%), HOMO → LUMO (60%)
	322	1.4057	H-2 → LUMO (22%), H-2 → L+2 (15%), HOMO → L+2 (29%)
S23	403	0.087	H-1 → L+1 (29%), HOMO → LUMO (46%)
	316	1.6608	H-2 → LUMO (32%), H-2 → L+2 (14%), HOMO → L+2 (26%)
S24	402	0.0066	H-1 → L+1 (31%), HOMO → LUMO (45%)
	315	1.9171	H-2 → LUMO (45%), H-2 → L+2 (11%), HOMO → L+3 (20%)

Table S3: Calculated Absorbance of BT*m*[10]CPP Compounds

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
***m*[10]CPP**	325	0.4002	H-1 → L+1 (16%), HOMO → LUMO (66%)
	298	2.8367	H-1 → LUMO (36%), HOMO → L+1 (36%)
13	365	0.4551	H-2 → LUMO (28%), H-1 → LUMO (34%), HOMO → LUMO (21%)
	297	2.3458	H-1 → L+1 (29%), HOMO → L+2 (31%)
14	393	0.5822	H-1 → LUMO (37%), HOMO → LUMO (46%)
	300	1.2704	H-2 → LUMO (18%),

			H-1 → L+1 (19%), HOMO → L+2 (12%)
15	394	0.552	H-1 → LUMO (28%), HOMO → LUMO (61%)
	287	1.5734	H-1 → L+1 (18%), HOMO → L+2 (34%)
16	400	0.5253	H-1 → LUMO (10%), HOMO → LUMO (74%)
	285	1.4175	H-1 → L+1 (20%), HOMO → L+2 (20%)
17	408	0.5311	H-2 → LUMO (13%), HOMO → LUMO (77%)
	317	1.378	H-1 → LUMO (23%), H-1 → L+1 (15%), HOMO → L+1 (36%)

Table S4: Calculated Absorbance of BT*m*[*n*]CPP Compounds

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
18	461	0.2519	HOMO → LUMO (94%)
	290	0.4523	H-4 → LUMO (10%), HOMO → L+2 (38%)
19	427	0.3687	HOMO → LUMO (85%)
	321	1.0384	H-1 → LUMO (61%), HOMO → L+1 (12%)
S25	472	0.1809	HOMO → LUMO (94%)
	279	0.3675	HOMO → L+2 (62%)
S26	438	0.323	HOMO → LUMO (88%)
	290	0.7514	H-1 → LUMO (13%), HOMO → L+1 (17%), HOMO → L+2 (34%)
S27	413	0.428	H-2 → LUMO (12%), HOMO → LUMO (77%)
	318	1.3515	H-1 → LUMO (43%), H-1 → L+1 (11%), HOMO → L+1 (19%)

Table S5: Calculated Absorbance of BT[*n*]CPP Compounds

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
S28	562	0.0297	HOMO → LUMO (92%)
	320	0.7094	H-2 → LUMO (77%), HOMO → L+2 (15%)
S29	463	0.0969	HOMO → LUMO (84%)
	317	0.8894	H-2 → LUMO (73%), HOMO → L+2 (16%)

S30	448	0.1688	H-1 → LUMO (13%), HOMO → LUMO (74%)
	325	0.9795	H-2 → LUMO (51%), H-1 → LUMO (15%), HOMO → L+2 (16%)
S31	420	0.3003	H-1 → LUMO (30%), HOMO → LUMO (62%)
	317	1.1495	H-2 → LUMO (60%), HOMO → L+2 (17%)
S32	406	0.3486	H-1 → LUMO (43%), HOMO → LUMO (45%)
	314	1.4229	H-2 → LUMO (48%), HOMO → L+2 (19%)

Table S6: Calculated Absorbance of *m*[10]CPP Compounds with Various Acceptors

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
20	425	0.3933	H-2 ⟶ LUMO (21%), HOMO ⟶ LUMO (70%)
	323	1.3091	H-5 ⟶ LUMO (11%), H-3 ⟶ LUMO (12%), H-1 ⟶ LUMO (43%)
21	460	0.5043	H-2 ⟶ LUMO (12%), HOMO ⟶ LUMO (81%)
	292	1.3119	H-1 ⟶ L+2 (16%), HOMO ⟶ L+1 (30%)
22	350	0.6011	HOMO ⟶ LUMO (76%)
	301	2.5044	H-1 ⟶ LUMO (22%), HOMO ⟶ L+1 (40%)
23	416	0.3128	H-2 ⟶ LUMO (21%), HOMO ⟶ LUMO (72%)
	290	1.8146	H-1 ⟶ LUMO (11%), H-1 ⟶ L+1 (22%), HOMO ⟶ L+2 (26%)
24	676	0.374	HOMO ⟶ LUMO (92%)
	305	1.7919	H-1 ⟶ L+1 (21%), HOMO ⟶ L+2 (27%)

Table S7: Calculated Absorbance of D-A Systems

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
a + g, opposite	407	0.5263	H-1 → LUMO (26%), HOMO → LUMO (60%)
	314	2.017	H-2 → LUMO (36%), HOMO → L+2 (24%)
a + g,	406	0.4539	H-1 → LUMO (31%),

adjacent			HOMO → LUMO (54%)
	317	1.6468	H-2 → LUMO (32%), H-2 → L+1 (11%), HOMO → L+2 (20%)
a + h, opposite	323	2.0884	H-2 → LUMO (10%), H-1 → L+1 (16%), HOMO → LUMO (18%), HOMO → L+2 (24%)
a + h, adjacent	449	0.6815	HOMO → LUMO (82%)
	309	1.3318	H-1 → LUMO (10%), H-1 → L+1 (20%), HOMO → L+2 (14%)
a + i, opposite	392	0.5471	H-1 → LUMO (52%), HOMO → LUMO (31%)
	313	2.023	H-3 → LUMO (22%), HOMO → L+2 (23%)
a + i, adjacent	401	0.5878	H-3 → LUMO (11%), HOMO → LUMO (60%)
	315	1.8159	H-3 → LUMO (20%), H-2 → LUMO (15%), H-2 → L+1 (10%), HOMO → L+2 (15%)
b + g, opposite	423	0.4017	H-1 → LUMO (40%), HOMO → LUMO (49%)
	318	1.8586	H-2 → LUMO (40%), H-2 → L+1 (10%), HOMO → L+2 (19%)
b + g, adjacent	432	0.388	H-2 → LUMO (22%), HOMO → LUMO (59%)
	332	1.5252	H-2 → LUMO (10%), H-1 → LUMO (28%), H-1 → L+1 (14%), HOMO → L+2 (18%)
b + h, opposite	326	1.5434	H-2 → LUMO (24%), HOMO → LUMO (25%), HOMO → L+2 (11%)
b + h, adjacent	548	0.5514	HOMO → LUMO (83%)
	305	1.4968	H-4 → LUMO (17%), H-2 → L+1 (10%), H-1 → L+1 (11%), H-1 → L+3 (10%), HOMO → L+2 (12%),

			HOMO → L+4 (10%)
b + i, opposite	412	0.4466	H-4 → LUMO (10%), H-1 → LUMO (48%), HOMO → LUMO (35%)
	321	3.1809	H-3 → LUMO (22%), H-2 → LUMO (13%), HOMO → L+2 (23%)
b + i, adjacent	416	0.4541	H-3 → LUMO (14%), H-2 → LUMO (15%), HOMO → LUMO (57%)
	322	1.5814	H-4 → LUMO (12%), H-3 → LUMO (19%), H-1 → LUMO (17%), HOMO → L+2 (15%)
c + g, opposite	446	0.5301	H-1 → LUMO (34%), HOMO → LUMO (53%)
	323	1.218	H-2 → LUMO (10%), H-2 → L+1 (11%), HOMO → L+1 (14%), HOMO → L+2 (14%)
c + g, adjacent	463	0.5801	H-1 → LUMO (37%), HOMO → LUMO (55%)
	309	1.1256	H-2 → LUMO (11%), H-2 → L+1 (20%), HOMO → L+2 (22%)
c + h, opposite	333	1.6504	H-2 → LUMO (23%), HOMO → LUMO (35%), HOMO → L+2 (10%)
c + h, adjacent	501	0.625	HOMO → LUMO (85%)
	312	1.562	H-1 → L+1 (25%), H-1 → L+2 (13%), HOMO → L+1 (10%), HOMO → L+3 (11%)
c + i, opposite	447	0.5571	H-1 → LUMO (50%), HOMO → LUMO (35%)
	323	1.5138	H-5 → LUMO (14%), H-3 → LUMO (39%), HOMO → L+2 (14%)
c + i, adjacent	443	0.5559	H-1 → LUMO (10%), HOMO → LUMO (63%)
	302	1.292	H-18 → LUMO (15%), H-2 → L+1 (11%), HOMO → L+2 (20%)

d + g, opposite	434	0.3729	H-1 → LUMO (29%), HOMO → LUMO (62%)
	292	1.0707	H-2 → LUMO (12%), H-2 → L+1 (20%), HOMO → L+2 (19%)
d + g, adjacent	423	0.3126	H-1 → LUMO (31%), HOMO → LUMO (55%)
	304	1.3146	H-2 → LUMO (10%), H-1 → L+1 (15%), HOMO → L+2 (26%)
d + h, opposite	373	1.1561	HOMO → L+1 (79%)
	325	1.1007	H-8 → LUMO (12%), H-2 → LUMO (21%), HOMO → LUMO (24%)
d + h, adjacent	418	0.3854	HOMO → LUMO (%), HOMO → LUMO (%)
	298	1.3915	H-2 → L+1 (18%), HOMO → L+2 (11%), HOMO → L+3 (10%)
d + i, opposite	372	0.6607	HOMO → LUMO (76%)
	324	1.799	H-2 → LUMO (12%), H-1 → LUMO (16%), HOMO → L+1 (26%), HOMO → L+2 (23%)
d + i, adjacent	431	0.4926	H-1 → LUMO (12%), HOMO → LUMO (72%)
	320	2.2175	H-4 → LUMO (15%), H-3 → LUMO (15%), HOMO → L+2 (21%)
e + g, opposite	350	0.324	HOMO → LUMO (58%), HOMO → L+2 (18%)
	305	2.6872	H-2 → LUMO (30%), HOMO → L+1 (35%)
e + g, adjacent	348	0.3019	HOMO → LUMO (22%), HOMO → L+1 (49%)
	303	2.6468	H-2 → LUMO (11%), H-1 → L+1 (14%), H-1 → L+2 (10%), HOMO → LUMO (15%), HOMO → L+3 (13%)
e + h, opposite	383	0.3687	H-1 → LUMO (45%), HOMO → LUMO (26%)

	321	2.7022	H-2 → LUMO (19%), H-1 → L+1 (19%), H-1 → L+2 (11%), HOMO → LUMO (10%), HOMO → L+3 (12%)
e + h, adjacent	372	0.6607	HOMO → LUMO (76%)
	324	1.799	H-2 → LUMO (12%), H-1 → LUMO (16%), HOMO → L+1 (26%), HOMO → L+2 (23%)
e + i, opposite	337	0.0651	H-1 → LUMO (16%), H-1 → L+1 (10%), HOMO → LUMO (24%), HOMO → L+1 (20%)
	311	2.0715	H-2 → LUMO (13%), H-1 → L+1 (20%), HOMO → LUMO (12%)
e + i, adjacent	336	0.3088	H-1 → LUMO (15%), HOMO → LUMO (16%), HOMO → L+1 (39%)
	305	2.5952	H-3 → LUMO (19%), H-1 → L+1 (24%), HOMO → LUMO (10%), HOMO → L+3 (11%)
f + g, opposite	661	0.3806	H-1 → LUMO (10%), HOMO → LUMO (86%)
	309	1.8317	H-2 → L+1 (15%), H-1 → L+1 (14%), HOMO → L+2 (27%)
f + g, adjacent	704	0.4	HOMO → LUMO (90%)
	305	1.9888	H-2 → L+1 (22%), HOMO → L+2 (18%), HOMO → L+4 (13%)
f + h, opposite	408	0.1839	H-3 → LUMO (19%), HOMO → LUMO (63%)
	318	1.7148	H-2 → L+1 (18%), H-1 → L+1 (12%), HOMO → L+2 (33%)
f + h, adjacent	774	0.4955	HOMO → LUMO (95%)
	319	1.5645	H-1 → L+1 (34%)
f + i,	660	0.4421	H-1 → LUMO (18%),

opposite			HOMO → LUMO (78%)
	310	0.5074	H-2 → L+1 (40%), H-2 → L+3 (15%)
f + i, adjacent	662	0.4435	HOMO → LUMO (88%)
	305	1.7353	H-2 → L+1 (16%), H-1 → L+2 (11%), HOMO → L+2 (20%)

Table S8: Calculated Absorbance of EDGs on *meta*-ring of *m*[6]CPP and *m*[10]CPP

Compound	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
***m*[6]CPP**	356	0.2042	HOMO → LUMO (87%)
	294	1.2167	H-1 → LUMO (31%), HOMO → L+1 (52%)
S39	377	0.2318	HOMO → LUMO (89%)
	299	1.4172	H-1 → LUMO (31%), HOMO → L+1 (50%)
S40	381	0.1857	H-1 → LUMO (15%), HOMO → LUMO (74%)
	306	1.1963	H-1 → LUMO (33%), HOMO → L+1 (35%)
S41	373	0.2721	HOMO → LUMO (91%)
	298	1.1163	H-3 → LUMO (15%), H-1 → LUMO (52%), H-1 → L+3 (11%), HOMO → L+1 (16%)
S42	554	0.2746	HOMO → LUMO (94%)
	351	1.667	H-2 → LUMO (24%), HOMO → L+1 (66%)
S43	334	0.254	H-2 → L+1 (11%), H-1 → LUMO (19%), HOMO → LUMO (45%)
	309	3.0451	H-2 → LUMO (17%), H-1 → LUMO (16%), HOMO → L+1 (43%)
S44	336	0.13	H-2 → L+1 (16%), H-1 → LUMO (41%), HOMO → LUMO (21%)
	314	2.7972	H-2 → LUMO (17%), H-1 → LUMO (11%), HOMO → L+1 (35%)
S45	302	3.0654	H-3 → LUMO (18%), H-2 → LUMO (13%), H-1 → L+1 (34%)

S46	326	0.336	H-2 → L+1 (15%), H-1 → LUMO (32%), HOMO → LUMO (36%)
	301	3.1351	H-2 → LUMO (30%), HOMO → L+1 (40%)

Table S9: Calculated Absorbance of [10]CPTcaq in Various Solvents

Solvent	Calc. Wavelength (nm)	Oscillator Strength	Major Contributions
Dichloro-methane	393	0.366	H-4 → LUMO (29%), H-2 → LUMO (42%), HOMO → LUMO (13%)
	308	1.1691	H-4 → L+1 (11%), H-2 → L+1 (17%), H-1 → LUMO (11%), HOMO → L+2 (18%)
Benzene	385	0.3873	H-4 → LUMO (23%), H-2 → LUMO (35%), HOMO → LUMO (25%)
	312	2.9976	H-1 → L+1 (13%), H-1 → L+2 (18%), HOMO → L+3 (17%)
Carbon Tetra-chloride	385	0.3827	H-4 → LUMO (23%), H-2 → LUMO (35%), HOMO → LUMO (26%)
	312	2.9872	H-1 → L+1 (13%), H-1 → L+2 (18%), HOMO → L+3 (17%)

4. Fluorescence Information of Calculated Compounds

Table S10: Calculated Fluorescence of Various Acceptors and Donors on [10]CPP

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
[10]CPP	467	0.6797	HOMO → LUMO (86%)
BT[10]CPP	594	0.6500	HOMO → LUMO (93%)
1	665	0.5326	HOMO → LUMO (71%), H-1 → LUMO (24%)
2	1085	0.3406	HOMO → LUMO (98%)
3	640	0.5163	HOMO → LUMO (93%)
4	697	0.5323	HOMO → LUMO (87%)
5	654	0.4543	HOMO → LUMO (93%)
6	585	0.6714	HOMO → LUMO (94%)
S1	521	0.9475	HOMO → LUMO (93%)
S2	604	0.7122	HOMO → LUMO (90%)
S3	636	0.5718	HOMO → LUMO (90%)
S4	454	1.0097	HOMO → LUMO (84%)
S5	610	0.755	HOMO → LUMO (94%)
S6	662	0.6334	HOMO → LUMO (95%)
S7	643	1.0341	HOMO → LUMO (96%)
S8	551	0.3684	HOMO → LUMO (60%), H-1 → LUMO (17%), H-3 → LUMO (14%)
S9	496	0.7618	HOMO → LUMO (84%)
S10	453	1.2874	HOMO → LUMO (82%)
S11	444	1.1816	HOMO → LUMO (86%)
S12	447	1.1255	HOMO->LUMO (85%)
S13	446	1.0669	HOMO → LUMO (86%)
S14	576	0.0716	HOMO → LUMO (39%), H-2 → LUMO (42%), H-4 → LUMO (12%)
S15	458	0.9471	HOMO → LUMO (87%)
S16	513	1.167	HOMO → LUMO (92%)

Table S11: Calculated Fluorescence of TT[*n*]CPP Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
7	1245	0.0087	HOMO → LUMO (98%)
8	794	0.0493	HOMO → LUMO (95%)
9	662	0.2857	HOMO → LUMO (94%)
10	618	0.4536	HOMO → LUMO (94%)
11	593	0.589	HOMO → LUMO (93%)

Table S12: Calculated Fluorescence of Dihedral Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
12	1245	0.0087	HOMO → LUMO (98%)
S17	794	0.0493	HOMO → LUMO (95%)
S18	662	0.2857	HOMO → LUMO (94%)
S19	618	0.4536	HOMO → LUMO (94%)

Table S13: Calculated Fluorescence of diBT[10]CPP Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
S20	638	0.7754	HOMO → LUMO (93%)
S21	608	0.7091	HOMO → LUMO (91%)
S22	606	0.6292	HOMO → LUMO (92%)
S23	608	0.6053	HOMO → LUMO (92%)
S24	609	0.5999	HOMO → LUMO (93%)

Table S14: Calculated Fluorescence of BT*m*[10]CPP Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
***m*[10]CPP**	463	0.9731	HOMO → LUMO (90%)
13	520	0.6906	HOMO → LUMO (85%)
14	550	0.6982	HOMO → LUMO (92%)
15	589	0.6844	HOMO → LUMO (94%)
16	615	0.595	HOMO → LUMO (95%)
17	614	0.5823	HOMO → LUMO (94%)

Table S15: Calculated Fluorescence of BT*m*[*n*]CPP Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
18	741	0.2581	HOMO → LUMO (98%)
19	653	0.4351	HOMO → LUMO (96%)
S25	677	0.3547	HOMO → LUMO (96%)
S26	798	0.1842	HOMO → LUMO (99%)
S27	637	0.515	HOMO → LUMO (95%)

Table S16: Calculated Fluorescence of BT[*n*]CPP Compounds

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
S28	1367	0.0143	HOMO → LUMO (97%)
S29	835	0.0917	HOMO → LUMO (95%)
S30	680	0.2975	HOMO → LUMO (93%)
S31	644	0.4341	HOMO → LUMO (93%)
S32	622	0.5288	HOMO → LUMO (92%)

Table S17: Calculated Fluorescence of *m*[10]CPP Compounds with Various Acceptors

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
20	677	0.4716	HOMO → LUMO (95%)
21	701	0.5004	HOMO → LUMO (95%)
22	608	0.6017	HOMO → LUMO (96%)
23	684	0.4167	HOMO → LUMO (96%)
24	1107	0.3198	HOMO → LUMO (99%)

Table S18: Calculated Fluorescence of D-A Systems

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
a + g, opposite	606	0.6129	HOMO → LUMO (93%)
a + g, adjacent	648	0.6545	HOMO → LUMO (94%)
a + h, opposite	597	0.6309	HOMO → LUMO (94%)
a + h, adjacent	659	0.768	HOMO → LUMO (95%)
a + i, opposite	587	0.7097	HOMO → LUMO (91%)
a + i, adjacent	578	0.6951	HOMO → LUMO (91%)
b + g, opposite	638	0.5007	HOMO → LUMO (92%)
b + g, adjacent	697	0.5388	HOMO → LUMO (94%)
b + h, opposite	648	0.5267	HOMO → LUMO (94%)
b + h, adjacent	725	0.6354	HOMO → LUMO (95%)
b + i, opposite	606	0.6105	HOMO → LUMO (90%)
b + i, adjacent	633	0.5645	HOMO → LUMO (92%)
c + g, opposite	692	0.518	HOMO → LUMO (94%)
c + g, adjacent	745	0.5546	HOMO → LUMO (95%)
c + h, opposite	688	0.5478	HOMO → LUMO (94%)
c + h, adjacent	762	0.6345	HOMO → LUMO (95%)
c + i, opposite	676	0.5888	HOMO → LUMO (92%)

c + i, adjacent	666	0.5905	HOMO → LUMO (92%)
d + g, opposite	631	0.4449	HOMO → LUMO (94%)
d + g, adjacent	677	0.4655	HOMO → LUMO (94%)
d + h, opposite	649	0.4654	HOMO → LUMO (95%)
d + h, adjacent	687	0.5616	HOMO → LUMO (95%)
d + i, opposite	645	0.4988	HOMO → LUMO (93%)
d + i, adjacent	603	0.4781	HOMO → LUMO (92%)
e + g, opposite	587	0.6884	HOMO → LUMO (95%)
e + g, adjacent	573	0.7887	HOMO → LUMO (94%)
e + h, opposite	517	1.0613	HOMO → LUMO (92%)
e + h, adjacent	615	0.8491	HOMO → LUMO (95%)
e + i, opposite	559	0.8044	HOMO → LUMO (95%)
e + i, adjacent	560	0.8439	HOMO → LUMO (94%)
f + g, opposite	1084	0.3424	HOMO → LUMO (99%)
f + g, adjacent	1161	0.366	HOMO → LUMO (99%)
f + h, opposite	1064	0.3615	HOMO → LUMO (99%)
f + h, adjacent	1193	0.4222	HOMO → LUMO (99%)
f + i, opposite	1029	0.3994	HOMO → LUMO (97%)
f + i, adjacent	1017	0.401	HOMO → LUMO (97%)

Table S19: Calculated Fluorescence of Linear Systems with Various Acceptors

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
S33	604	1.1256	HOMO → LUMO (94%)
S34	517	1.4117	HOMO → LUMO (92%)
S35	541	1.0497	HOMO → LUMO (92%)
S36	819	0.6745	HOMO → LUMO (97%)
S37	497	1.9058	HOMO → LUMO (94%)
S38	524	0.7436	HOMO → LUMO (90%)

Table S20: Calculated Fluorescence of Linear D-A Systems

Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
a + g, linear	584	1.4641	HOMO → LUMO (95%)
a + h, linear	581	1.6939	HOMO → LUMO (94%)
a + i, linear	532	1.4373	HOMO → LUMO (92%)
b + g, linear	604	1.1519	HOMO → LUMO (95%)
b + h, linear	611	1.3217	HOMO → LUMO (94%)
b + i, linear	558	1.0923	HOMO → LUMO (92%)
c + g, linear	659	1.1709	HOMO → LUMO (95%)
c + h, linear	669	1.3425	HOMO → LUMO (95%)
c + i, linear	621	1.1703	HOMO → LUMO (93%)
d + g, linear	610	0.9409	HOMO → LUMO (95%)
d + h, linear	599	1.114	HOMO → LUMO (94%)
d + i, linear	534	0.8399	HOMO → LUMO (91%)
e + g, linear	533	2.0954	HOMO → LUMO (95%)
e + h, linear	537	2.3079	HOMO → LUMO (94%)
e + i, linear	500	2.1001	HOMO → LUMO (94%)
f + g, linear	954	0.7562	HOMO → LUMO (98%)
f + h,	975	0.8636	HOMO → LUMO (98%)

linear			
f + i, linear	848	0.7196	HOMO → LUMO (97%)

Table S21: Calculated Fluorescence of EDGs on *meta*-ring of *m*[6]CPP and *m*[10]CPP

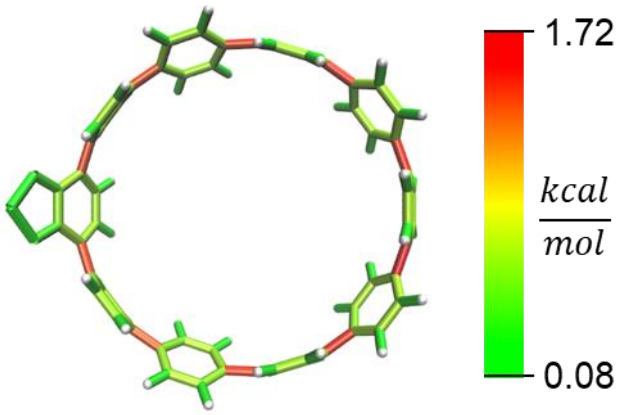
Compound	Calculated Emission (nm)	Oscillator Strength	Major Contributions
***m*[6]CPP**	544	0.3437	HOMO → LUMO (95%)
S39	551	0.3014	HOMO → LUMO (95%)
S40	567	0.2132	HOMO → LUMO (92%)
S41	543	0.3566	HOMO → LUMO (96%)
S42	554	0.2746	HOMO → LUMO (94%)
S43	464	0.9227	HOMO → LUMO (88%)
S44	464	0.9008	HOMO → LUMO (82%)
S45	468	0.9251	HOMO → LUMO (90%)
S46	471	0.9055	HOMO → LUMO (89%)

Table S22: Calculated Fluorescence of [10]CPTcaq in Various Solvents and solvation methods

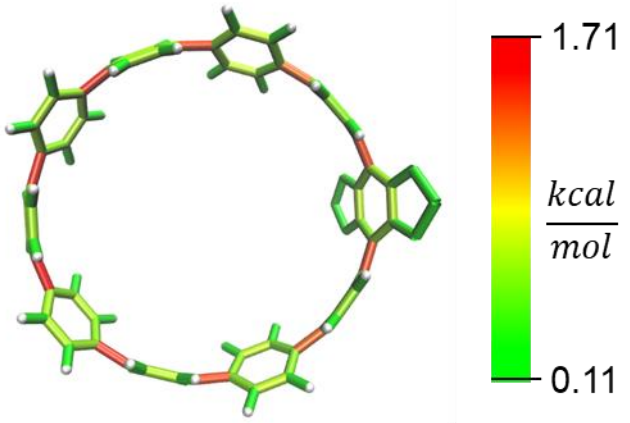
Solvent	Calculated Emission (nm)	Oscillator Strength	Major Contributions
Dichloro-methane	526	0.6076	H-2 → LUMO (18%), H-1 → LUMO (20%), HOMO → LUMO (42%)
Benzene	508 (529 nm using state-specific solvation)	0.5456	H-2 → LUMO (21%), H-1 → LUMO (28%), HOMO → LUMO (26%)
Carbon Tetra-chloride	506 (529 nm using state-specific solvation)	0.5338	H-4 → LUMO (11%), H-2 → LUMO (25%), H-1 → LUMO (24%), HOMO → LUMO (26%)

5. StrainViz Calculations

Strain energy analysis was performed using StrainViz.[1] All data relevant to this analysis is available in StrainViz.zip. Pictures of each strain energy map are shown below.



BT[10]CPP



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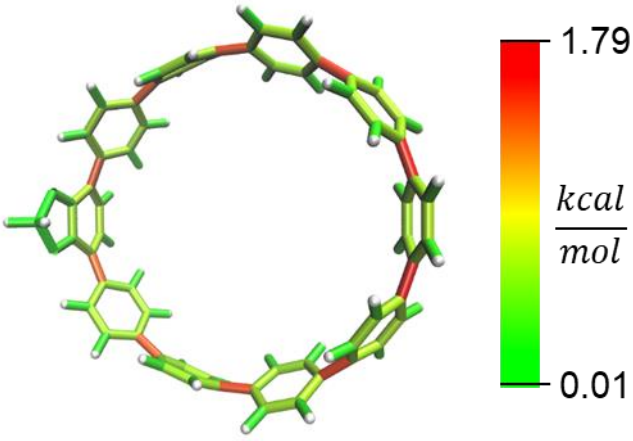

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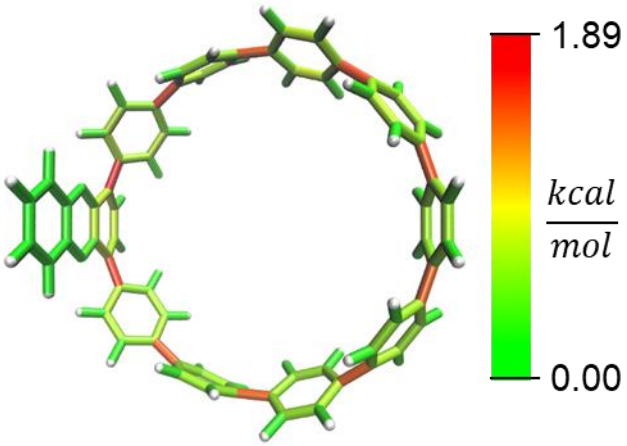

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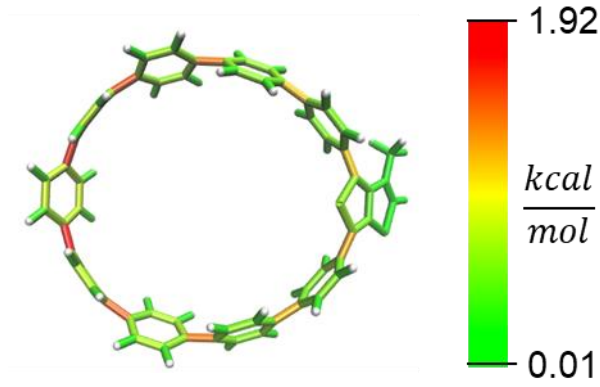

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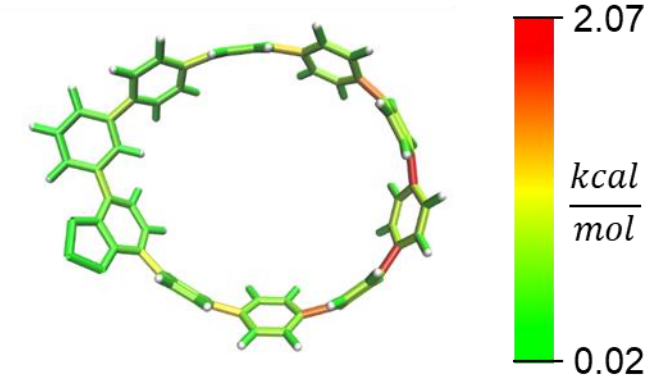

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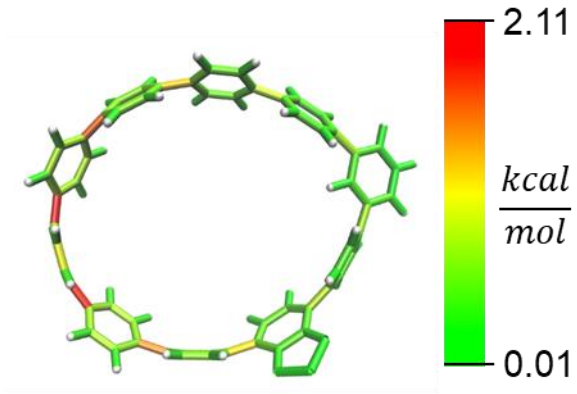

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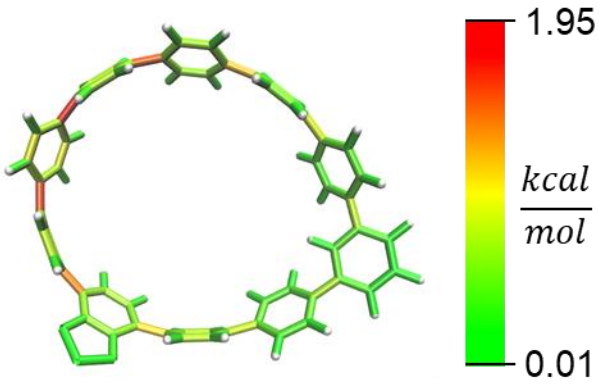

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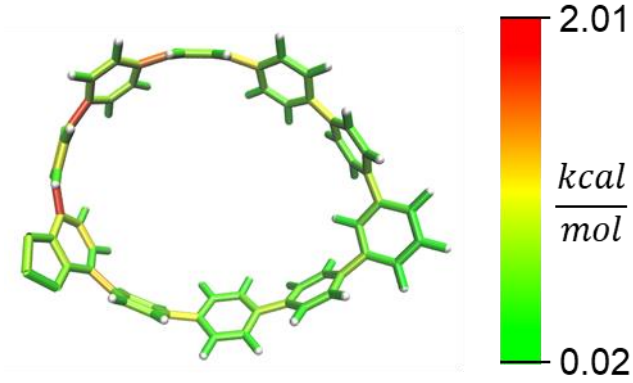

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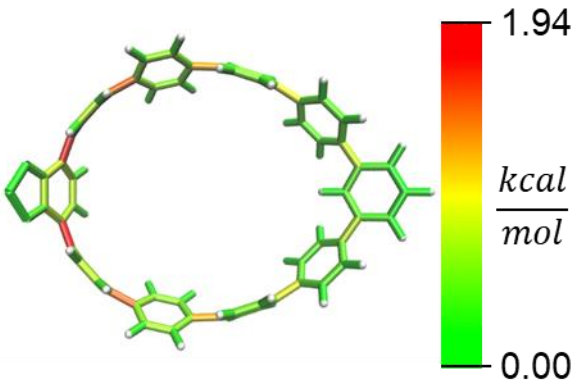

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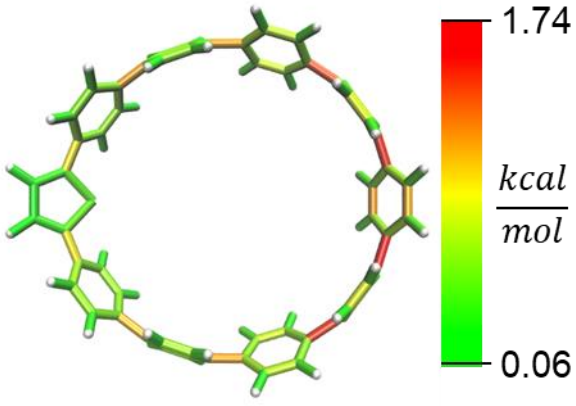

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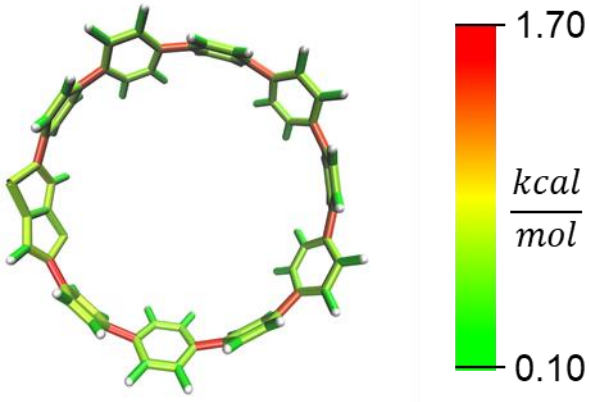

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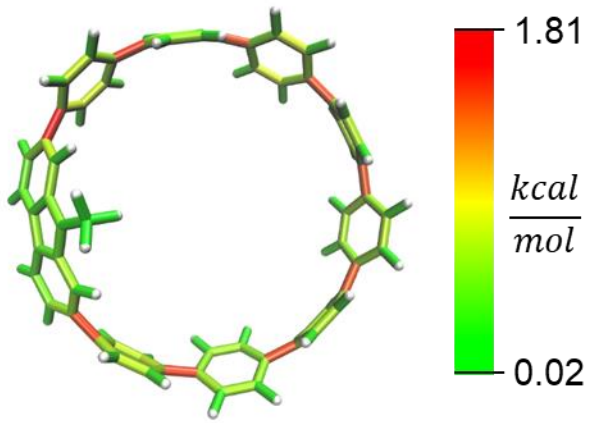

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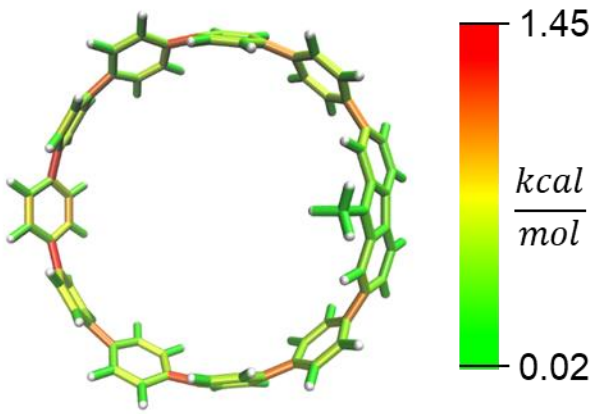


Donor i

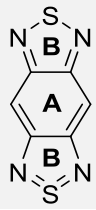
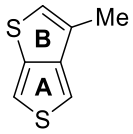
6. NICS Calculations

Nucleus independent chemical shift (NICS) calculations were performed for some electronic modulating units. Aromaticity is a factor explaining only part of the electronic modulating unit effect, therefore only a handful of calculations of this type were performed.

The software package Aroma[2] was used to perform these calculations. Electron accepting units **BT**, **2**, **4**, **5**, and **6** were analyzed. The out of plane component of the magnetic field was measured at the center of each ring and at 1 angstrom from the center.

Table S23: NICS values for electronic modulating units.

Compound	Structure	Center	NICS(0)	NICS(1)
Benzene		A	-14.1	-29.1
a		A	-5.8	-22.1

		B	-22.5	-37.4
f		A	-14.5	-29.5
		B	-22.3	-37.2
c		A	14.1	-4.8
		B	2.2	-19.7
d		A	-11.3	-26.3
		B	-16.4	-33.2
e		A	-6.0	-27.4
		B	12.0	-12.3

7. References

(1) Colwell, C. E.; Price, T. W.; Stauch, T.; Jasti, R. *Chem. Sci.* **2020**, *11*, 3923–3930.

(2) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883–893.