Supporting information

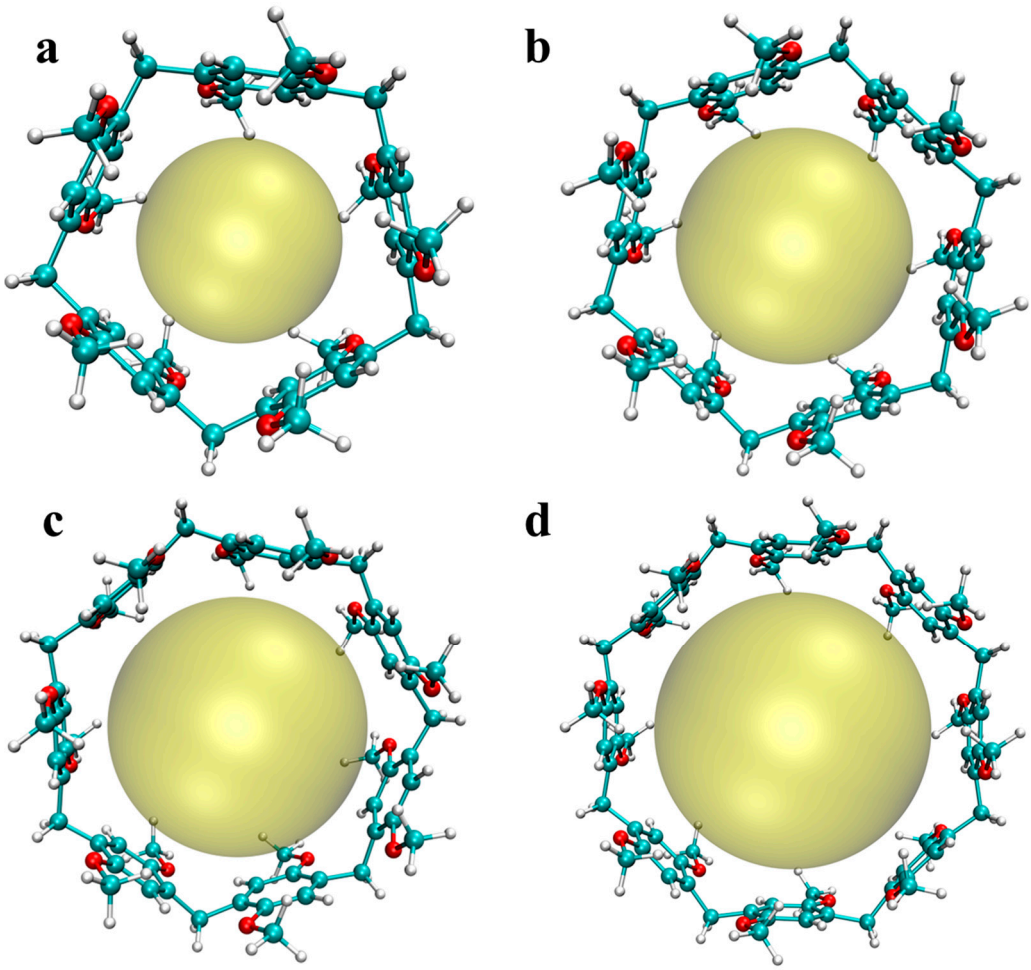


Figure S1: Schematic diagram of the molecular pore of pillar[n]arene.

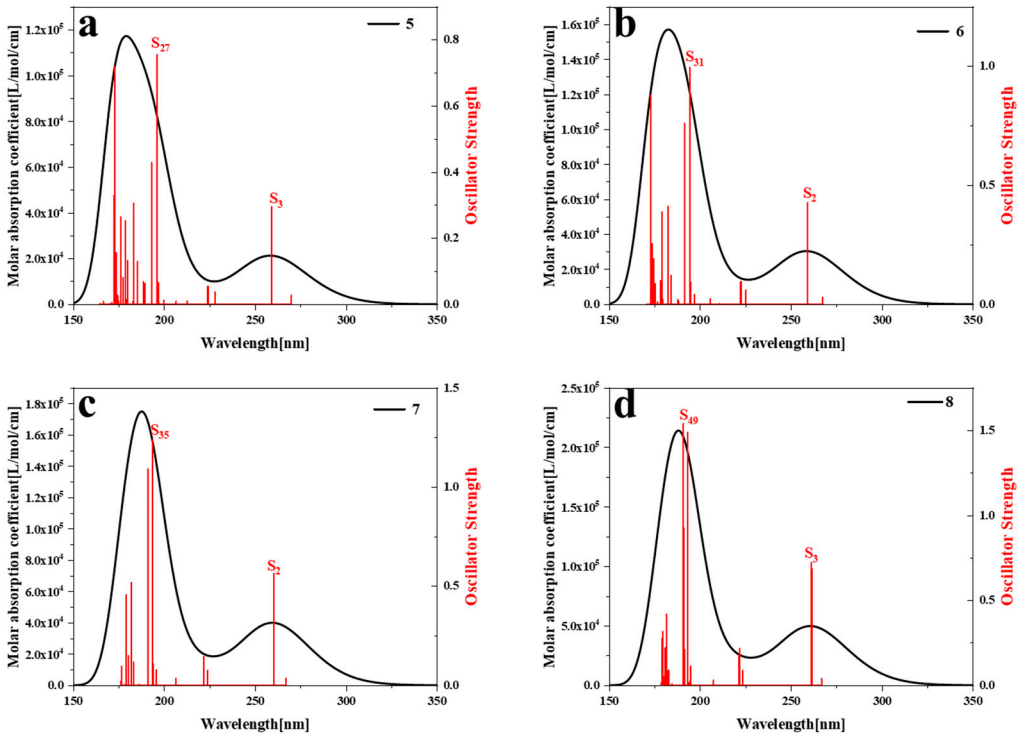


Figure S2: OPA spectrums of pillar[n]arene.

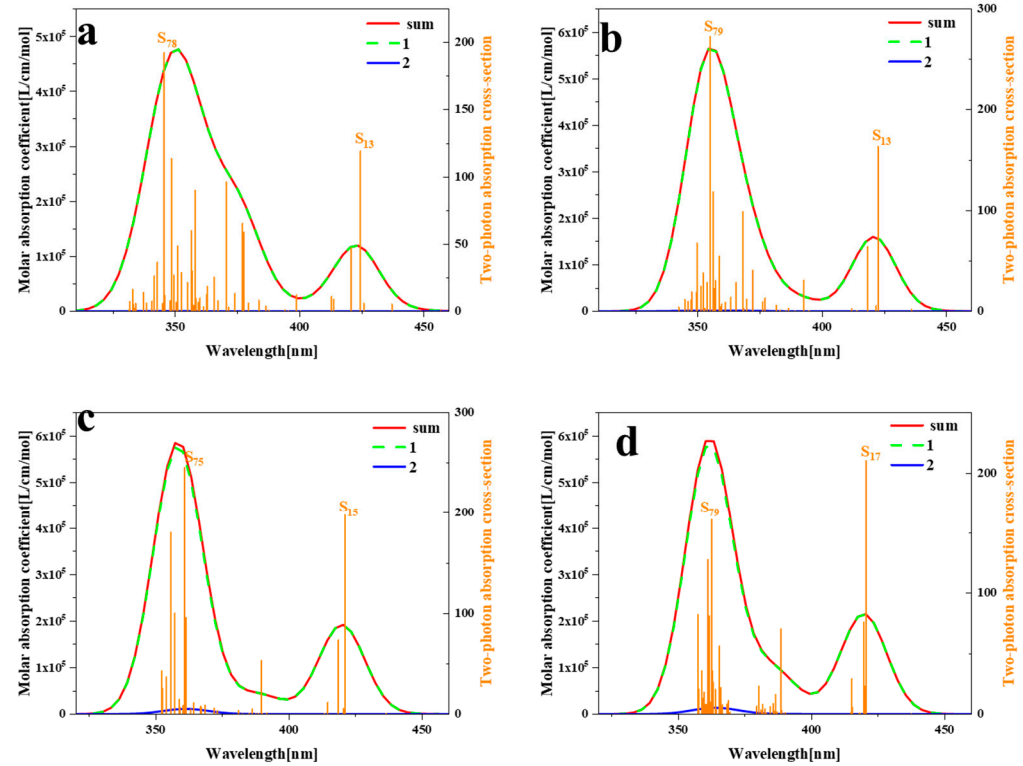


Figure S3: TPA spectrums of pillar[n]arene.

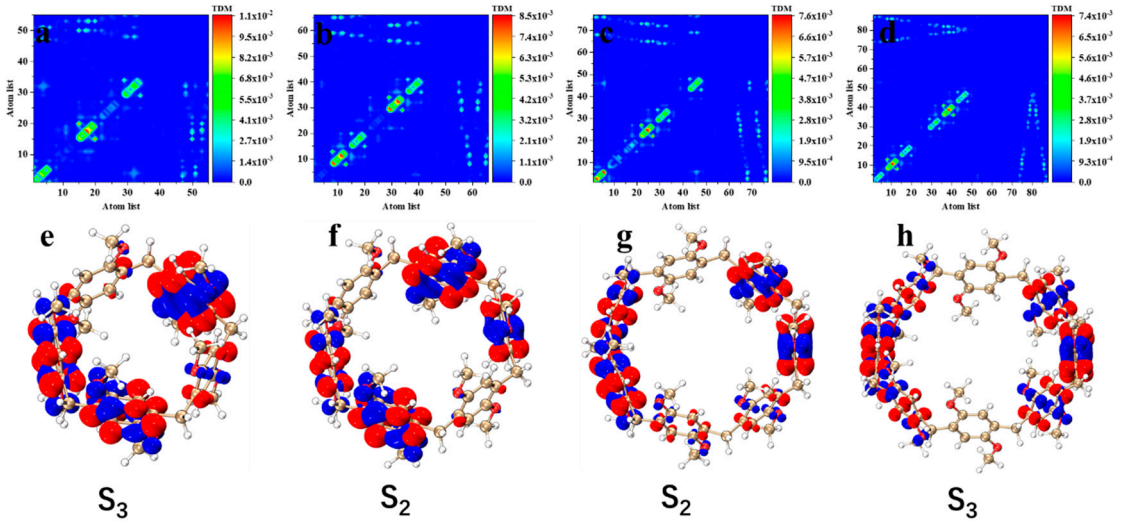
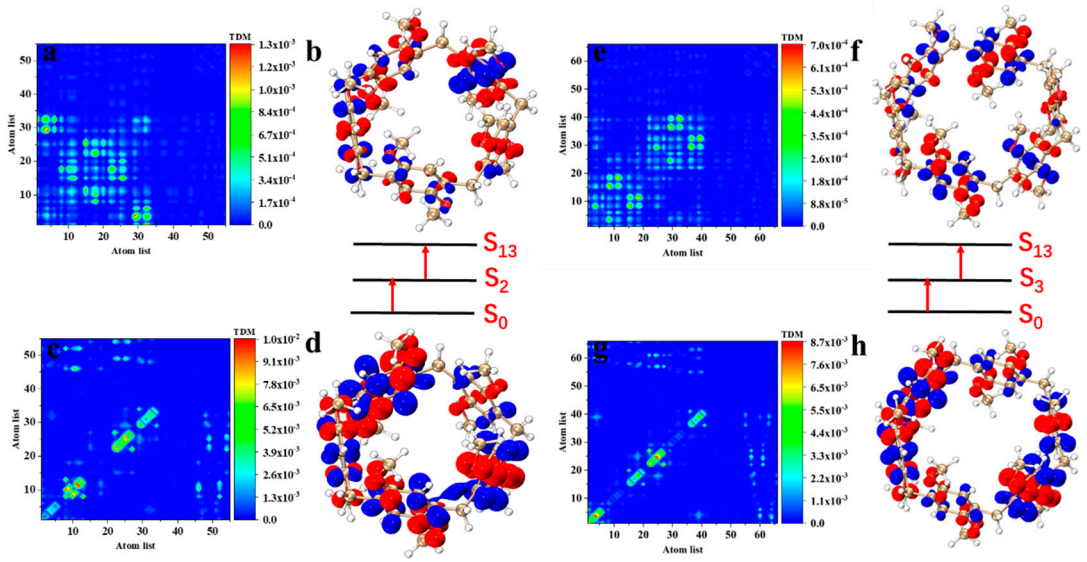
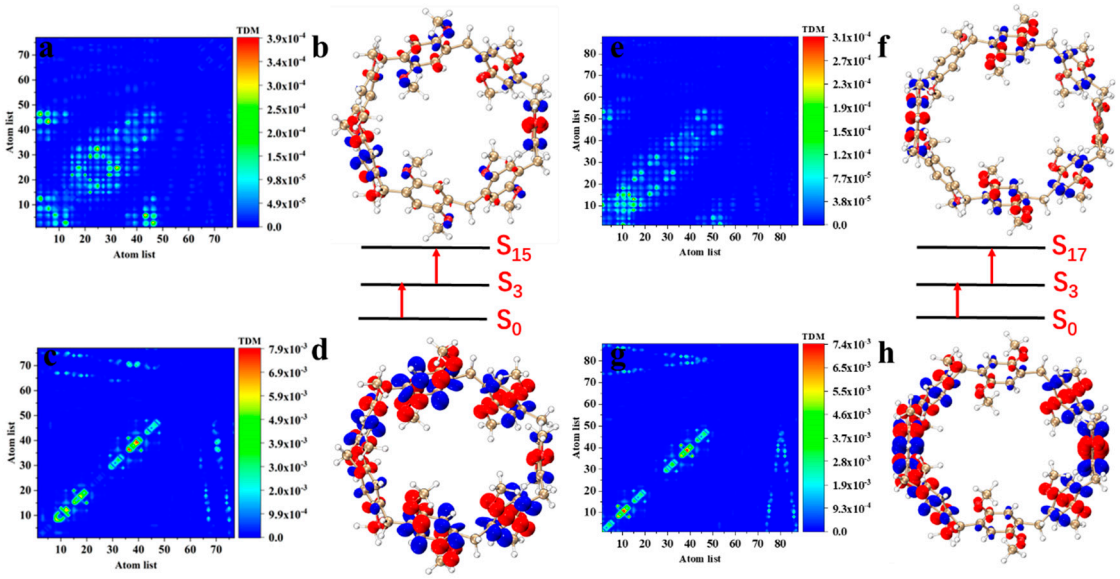


Figure S4. pillar[n]aren's TDM and electron hole pair density (e-h) of absorption peak excited states S3(a), S2(b), S2(c) and S3(d) near 230nm-300nm, respectively.



FigureS5. pillar[5]arene two-step transition process in S_{13}, from ground state to intermediate state (c) and from intermediate state to final state (a) TDM and electron hole pair density (d, b); pillar[6]arene two-step transition process in S_{13}, from the ground state to the intermediate state (g) and from the intermediate state to the final state (e) TDM and electron hole pair density (h, f).



FigureS6. pillar[7]arene two-step transition process in S_{15}, from ground state to intermediate state (c) and from intermediate state to final state (a) TDM and electron hole pair density (d, b); pillar[8]arene two-step transition process in S_{17}, from the ground state to the intermediate state (g) and from the intermediate state to the final state (e) TDM and electron hole pair density (h, f).

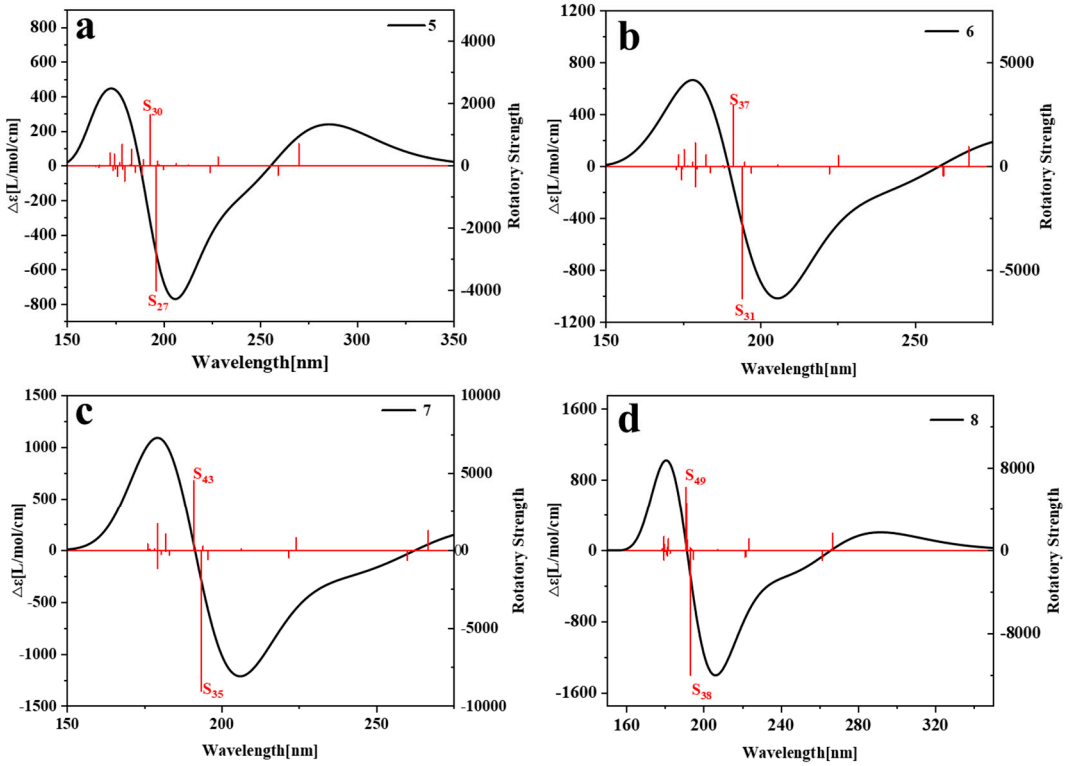


Figure S7. ECD spectra of pillar[n]arene.

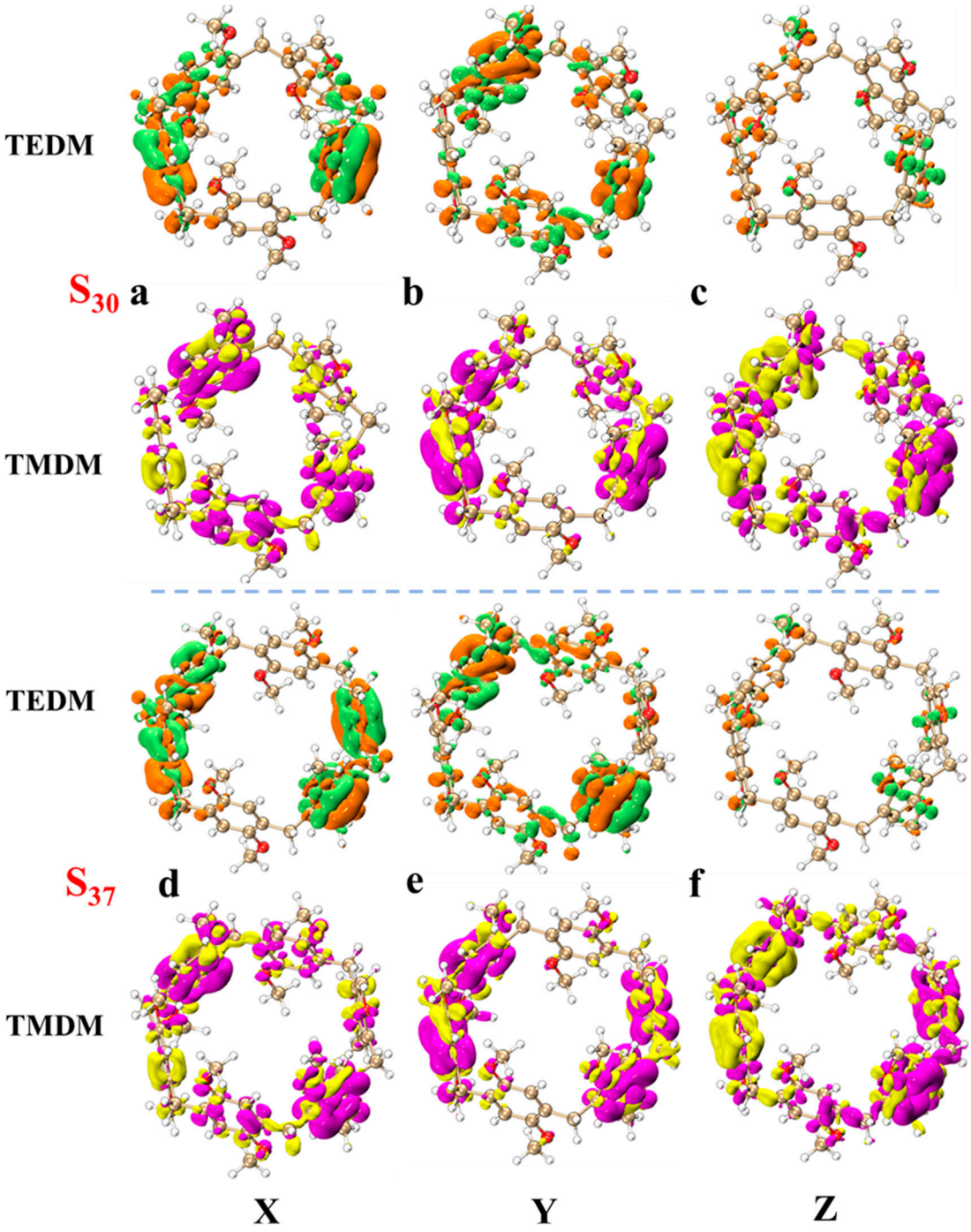


Figure S8. The TEDM and TMDM (a-c) of the major ECD excited states of pillar[5]arene near 150-190nm. The TEDM and TMDM (d-f) of the major ECD excited states of pillar[6]arene near 150-190nm.

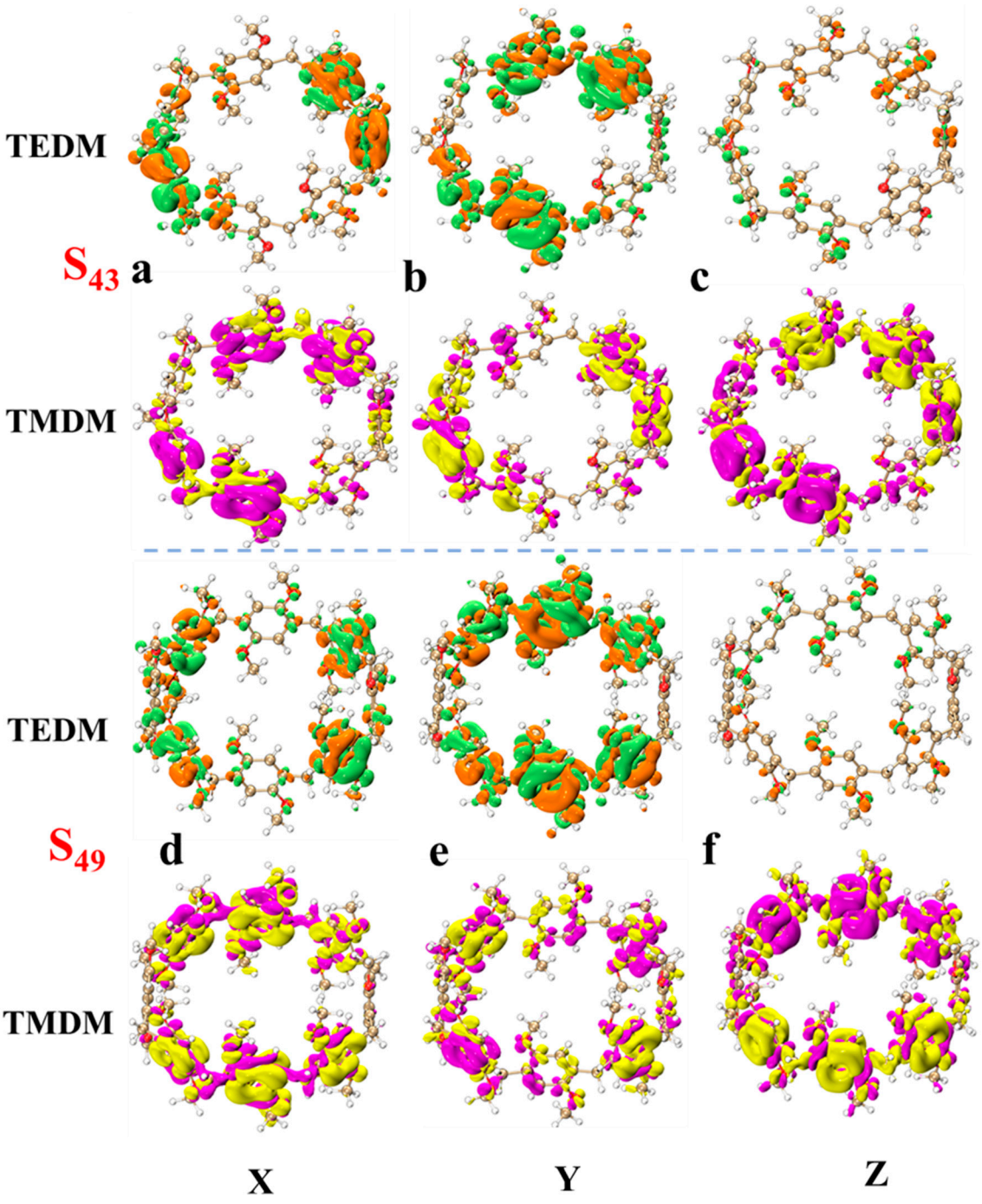


Figure S9. The TEDM and TMDM (a-c) of the major ECD excited states of pillar[7]arene near 150-190nm. The TEDM and TMDM (d-f) of the major ECD excited states of pillar[8]arene near 150-190nm.

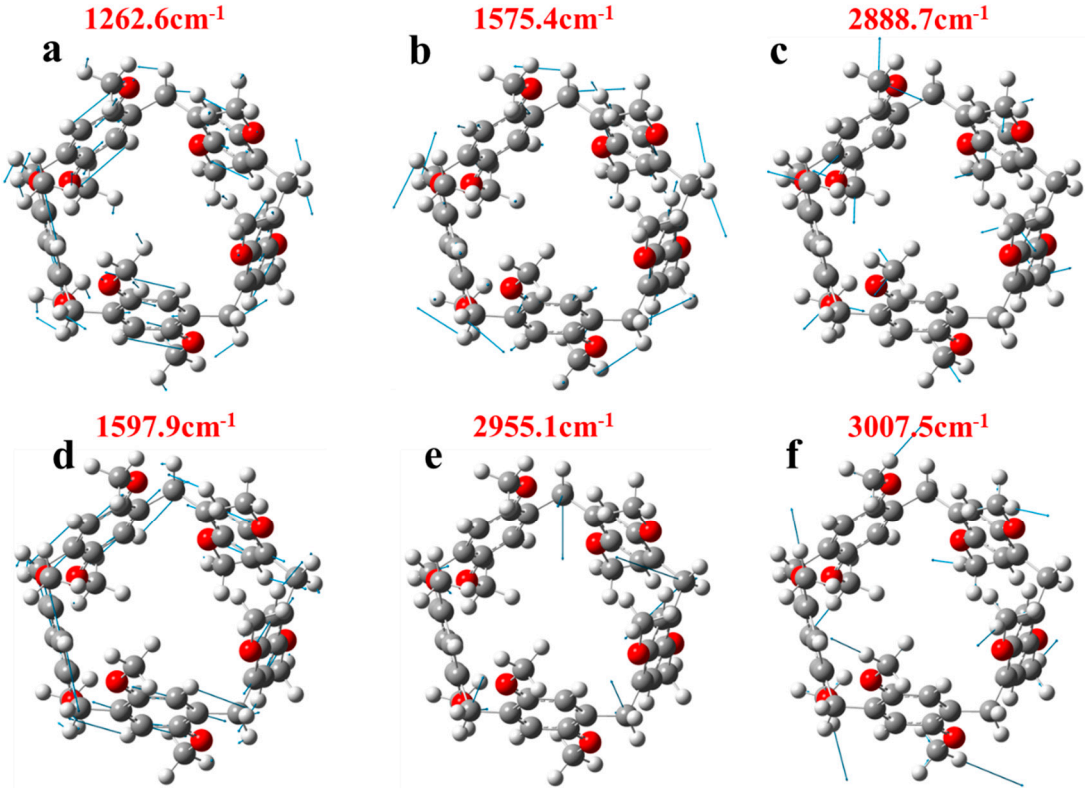


Figure S10. The vibration pattern of pillar[5]arene at the peak of Raman absorption.

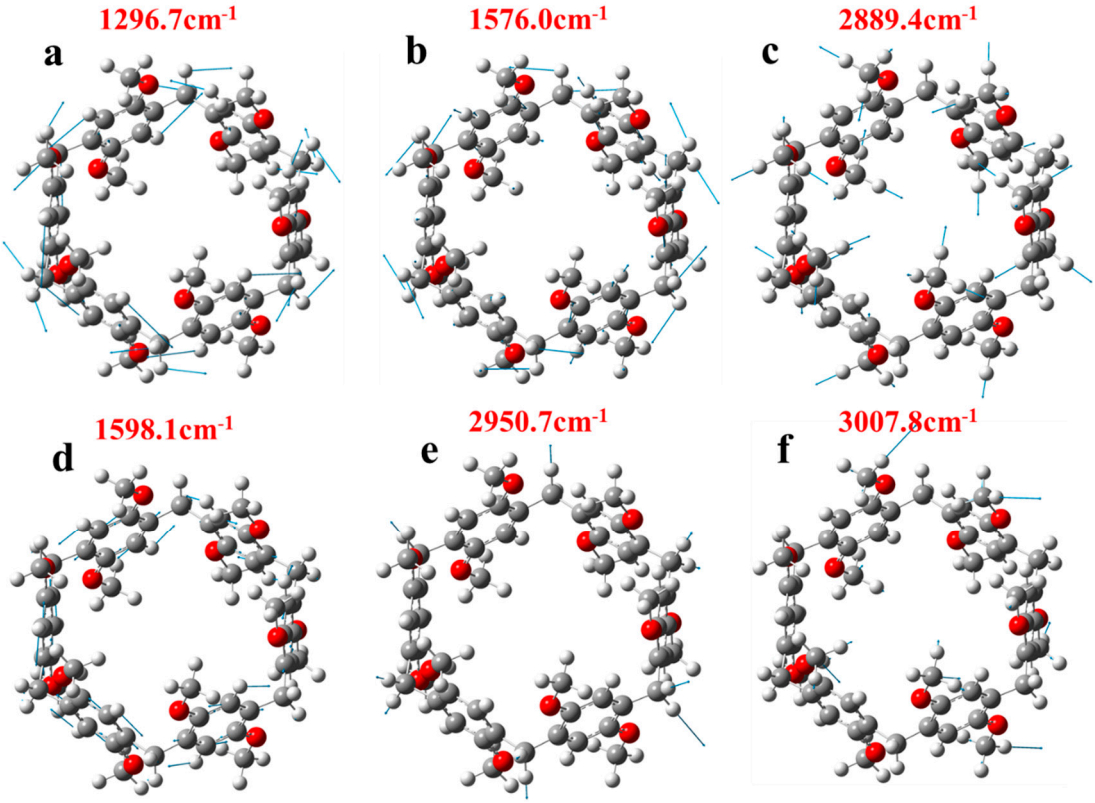


Figure S11. The vibration pattern of pillar[6]arene at the peak of Raman absorption.

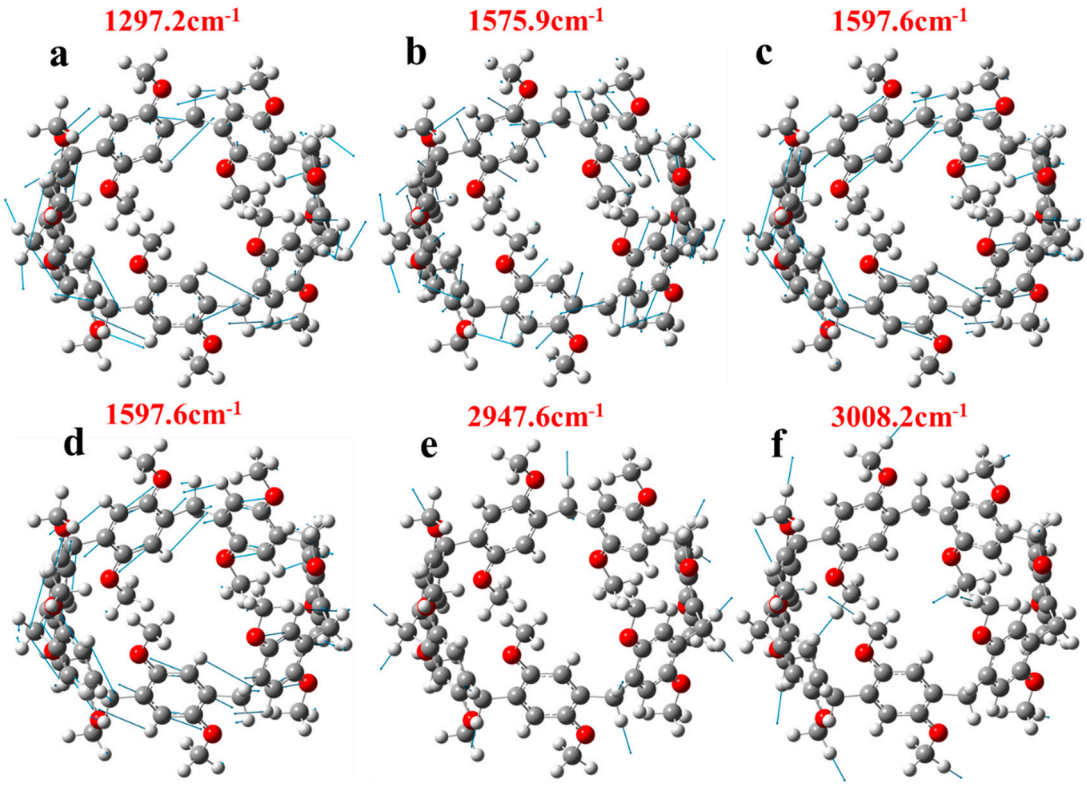


Figure S12. The vibration pattern of pillar[7]arene at the peak of Raman absorption.

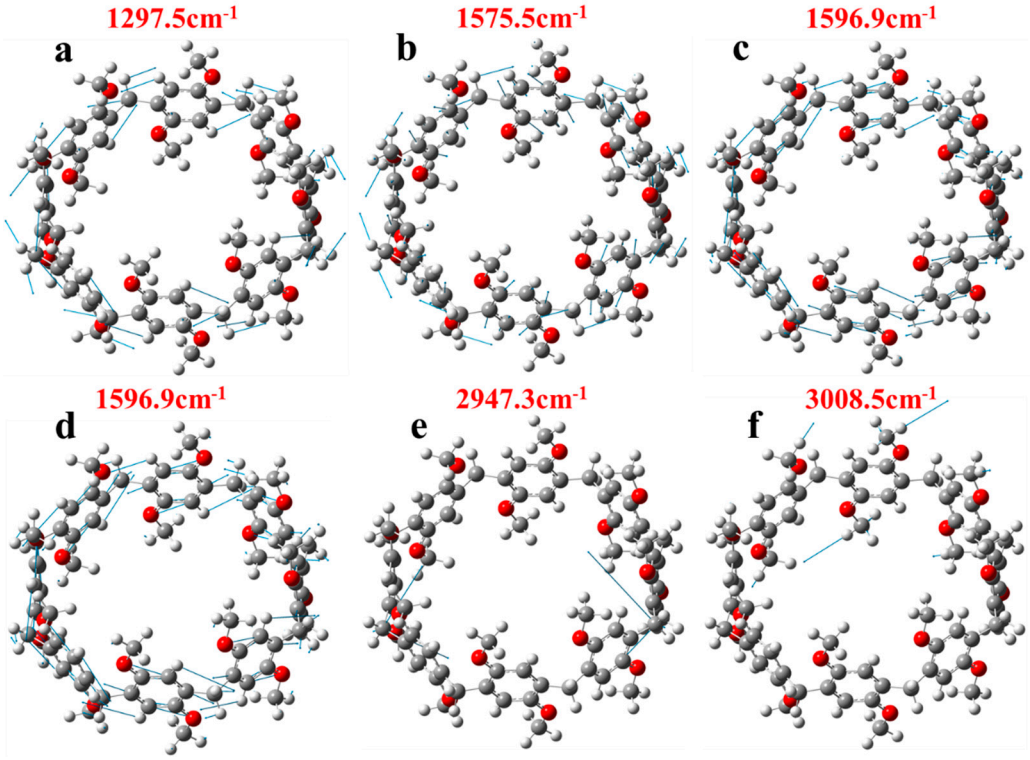


Figure S13. The vibration pattern of pillar[8]arene at the peak of Raman absorption.

Table S1. pillar[n]arene main excited state transition index of absorption peak near 230nm-300nm.

Molecule	Excited states	Oscillator Strength	Excited energy(eV)	H(Å)	D(Å)	t (Å)	Sr
pillar[5]arene	S_3	0.2959	4.788	4.614	0.005	-1.548	0.81032
pillar[6]arene	S_2	0.4271	4.786	5.430	0.008	-3.524	0.80260
pillar[7]arene	S_2	0.5653	4.769	6.263	0.002	-2.226	0.79582
pillar[8]arene	S_3	0.6880	4.749	7.105	0.003	-5.042	0.79208

Table S2. pillar[n]arene's transition dipole moment and absorption cross section of two-photon absorption excited state at 400-450nm.

Molecule	State	Process	Integral value(Debye)
pillar[5]arene	S13	$\langle\phi_{s0}\|\mu\|\phi_{s2}\rangle\times\langle\phi_{s2}\|\mu\|\phi_{s13}\rangle$	2.57×2.75
pillar[6]arene	S13	$\langle\phi_{s0}\|\mu\|\phi_{s3}\rangle\times\langle\phi_{s3}\|\mu\|\phi_{s13}\rangle$	3.71×2.43
pillar[7]arene	S15	$\langle\phi_{s0}\|\mu\|\phi_{s3}\rangle\times\langle\phi_{s3}\|\mu\|\phi_{s15}\rangle$	4.93×2.11
pillar[8]arene	S17	$\langle\phi_{s0}\|\mu\|\phi_{s3}\rangle\times\langle\phi_{s3}\|\mu\|\phi_{s17}\rangle$	6.36×1.91

Table S3 TEDM/TMDM values and tensor product eigenvalues of pillar[n]arene near 150-190nm.

		X	Y	Z	Eigenvalue
pillar[5]arene	TEDM	-0.7275	-1.4806	-0.0012	6.9575
S30	TMDM	1.8640	3.7832	-0.0022	
pillar[6]arene	TEDM	-1.0943	-1.8896	-0.0005	12.7010
S37	TMDM	2.9121	5.0351	-0.0038	
pillar[7]arene	TEDM	-1.9339	1.7687	-0.0001	19.3562
S43	TMDM	5.4511	-4.9835	-0.0008	
pillar[8]arene	TEDM	3.1032	0.2103	0.0024	26.3702
S49	TMDM	-8.4583	-0.5823	0.0178	