Supplementary Information

Electronic Structure of Cycloparaphenylenes Directly Observed by Photoemission Spectroscopy

Kaname Kanai[1,*], Takuya Inoue[1], Takaya Furuichi[1], Kaito Shinoda[1], Takashi Iwahashi[2], Yukio Ouchi[2]

[1]*Department of Physics, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan,*
[2] *Department of Materials Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

Methods

The MO calculations for the isolated molecules based on DFT were performed using Gaussian 09 with B3LYP parameters and the 6-31G(d) basis set. The simulated UPS (Occ.) and IPES (Unocc.) spectra were obtained by broadening the calculated MOs with a Gaussian function with 0.5 eV FWHM to reproduce the observed spectra.

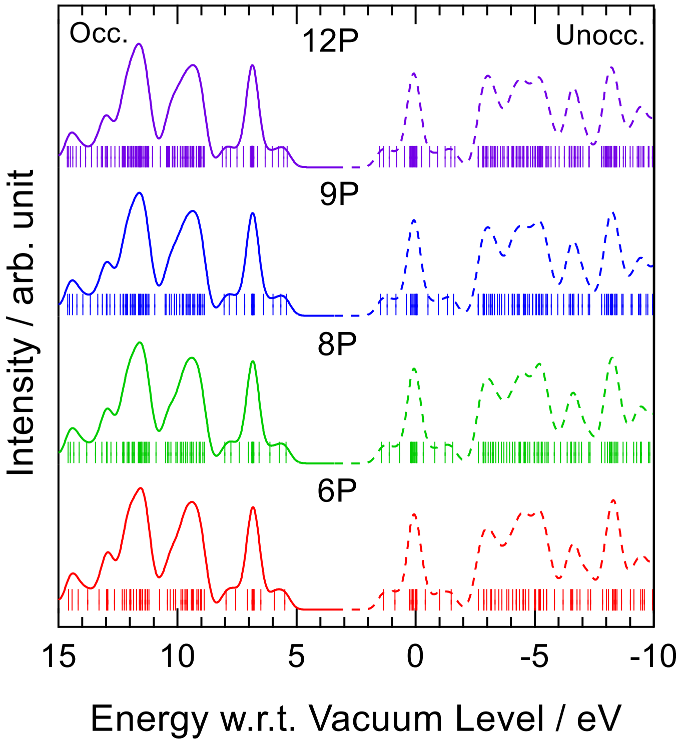

Fig. S1 The vertical bars present the calculated MOs of *n*Ps (*n* = 6, 8, 9, and 12). The solid and dashed lines are the simulated UPS (Occ.) and IPES (Unocc.) spectra based on the MO calculation results, respectively. The bottom axis represents the energy measured from the vacuum level.

The overall features of the simulated spectra for *n*P are very similar for all *n*, indicating little dependence of electronic structure on *n* over 6, except for the size of the HOMO–LUMO gap. Thus, the molecular structure of *n*P is nearly unchanged for *n* larger than 6.

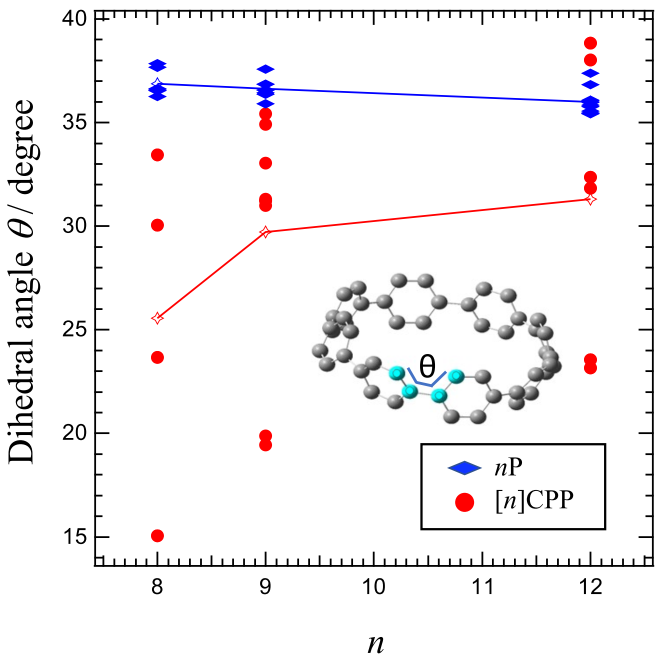

Fig. S2 Calculated dihedral angle *θ* plotted as a function of *n* for *n*P and [*n*]CPP (*n* = 8, 9, and 12). The open diamonds connected by solid lines represent the average values of *θ* for each *n*.

Fig. S2 shows the dihedral angle *θ* plotted against *n* for *n*P and [*n*]CPP (*n* = 8, 9, and 12). The model of [8]CPP shown in the figure defines *θ*. Scattering data for each *n* represent the values of *θ* for each dihedral angle between two neighboring phenylene units. The open diamonds connected by solid lines show the average value of *θ* for each *n*. *θ* for *n*P remains around 36 degrees and there is little dependence of *θ* on *n*, although the average value slightly decreases as the molecular size increases. On the other hand, the average value of *θ* of [*n*]CPP rapidly increases and approaches the average value of *θ* for *n*P with increasing *n*. In small diameter molecules with *n* less than 10, neighboring phenylene units can twist only slightly owing to steric hindrance, which raises the strain energy. In distorted molecules with large *n*, the overlaps between wave functions of π-orbitals decrease and π-conjugation length decreases, leading to an increase in the HOMO–LUMO gap.

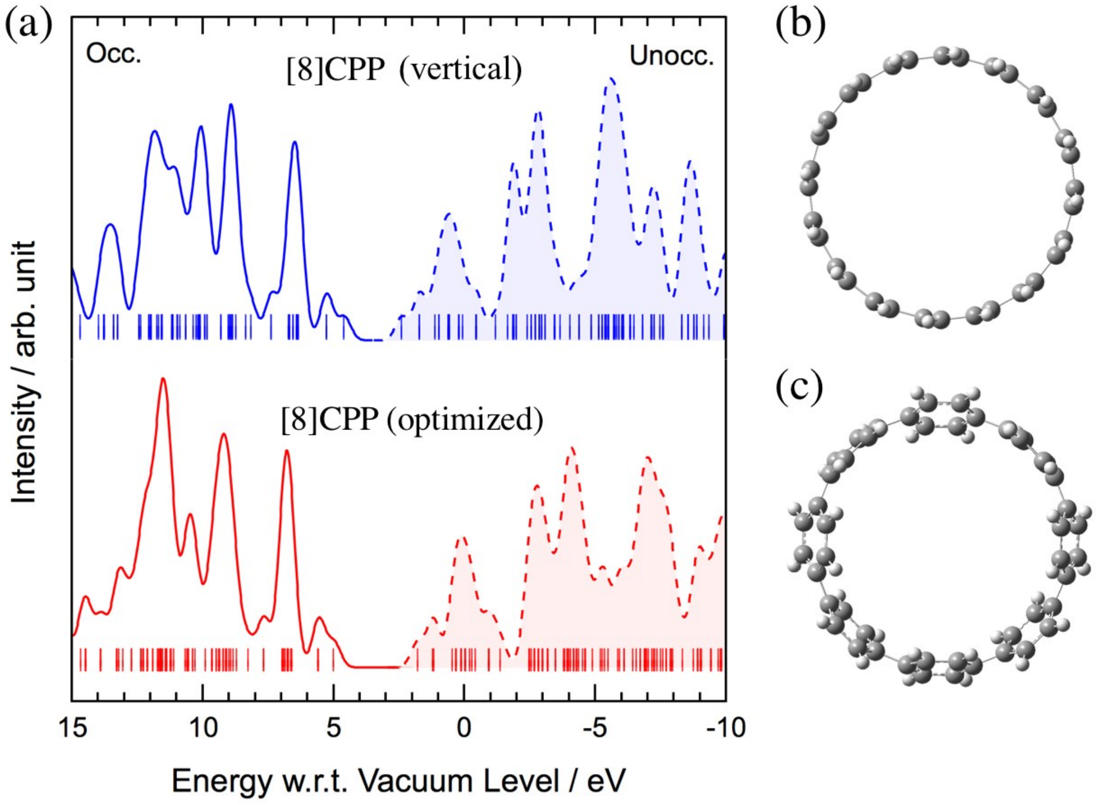

Fig. S3 (a) Calculated MOs and the simulated spectra for [8]CPP with vertical conformations of each phenylene unit (vertical structure) and the optimized structure. (b) and (c) show aerial views of the vertical and optimized structures. In structures with vertical conformations, every θ is zero.

The effects caused by bending the C–C bonds connecting each phenylene group are shown by the calculated MOs and the simulated spectra for [8]CPP in vertical conformations and for optimized structures given in Fig. S3. In the vertical structure, all the θ angles between neighboring phenylene groups are set to zero, meaning each phenylene group does not rotate. This is a virtual structure because the strain energy overwhelms the energy gain by delocalization of the π-electrons. Nonetheless, comparison between the vertical and optimized structures is helpful in understanding the effects of bending the C–C bonds in [*n*]CPP on their electronic structure. The optimized structure was obtained by a balance between the strain energy and the stabilization energy of the π-electron system. Fig. S3(a) compares the electronic structure of the vertical and optimized structures of [8]CPP shown in Figs. S3(b) and

S3(c). Both the occupied and unoccupied electronic structures of vertical [8]CPP differ from those of the optimized structure. This indicates that the strain in [*n*]CPP molecules, such as the rotation of the C–C bonds, markedly affects the electronic structure. The HOMO–LUMO gap of [8]CPP with the vertical structure is about 1 eV smaller than that of the optimized structure. The small HOMO–LUMO gap of the vertical structure originates from the large overlap between the π-orbitals on neighboring phenylene units, leading to π-conjugation throughout [8]CPP. The π-conjugation length is reduced in the optimized structure by the strain inside the molecule widening the HOMO–LUMO gap.