

Electronic Supplementary Information

**Charge-transfer complexes based on C_{2v} -symmetric
benzo[*ghi*]perylene: comparison of their dynamic and electronic
properties with those of D_{6h} -symmetric coronene**

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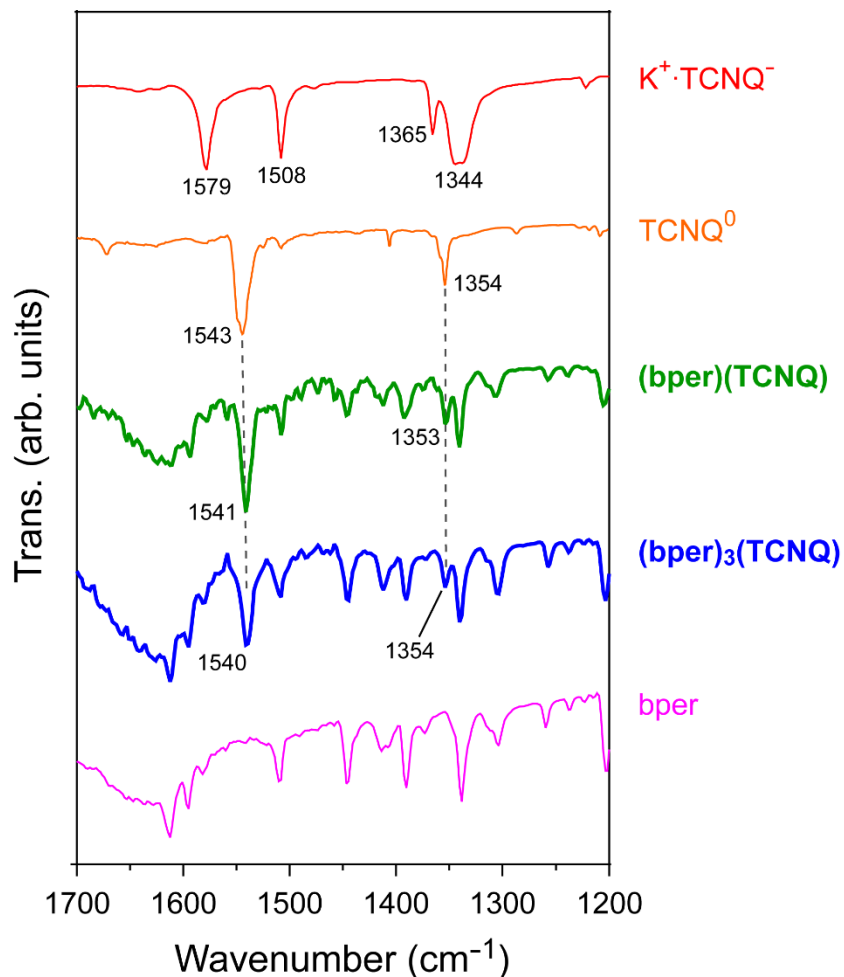


Fig. S1 Infrared spectra of (bper)(TCNQ) (**1**; green) and (bper)₃(TCNQ) (**3**; blue) together with monoanionic TCNQ (red), neutral TCNQ (orange), and neutral bper (pink), measured in dispersed KBr pellets. The $\nu_{\text{C}=\text{C}}$ modes of **1** (1541 cm^{-1}) and **3** (1540 cm^{-1}) are comparable to that of neutral TCNQ (1543 cm^{-1}). Assuming that the charge state of TCNQ molecule is linearly correlated with the $\nu_{\text{C}=\text{C}}$ shift, $-(\omega_{\text{obs}} - \omega_0)/(\omega_1 - \omega_0)$, where ω_{obs} , ω_0 , and ω_1 are the $\nu_{\text{C}=\text{C}}$ mode frequencies of a CT complex, a neutral TCNQ, and a monoanionic TCNQ, respectively,¹ the charge states of the TCNQ molecules in **1** and **3** were estimated to be less than -0.1 .

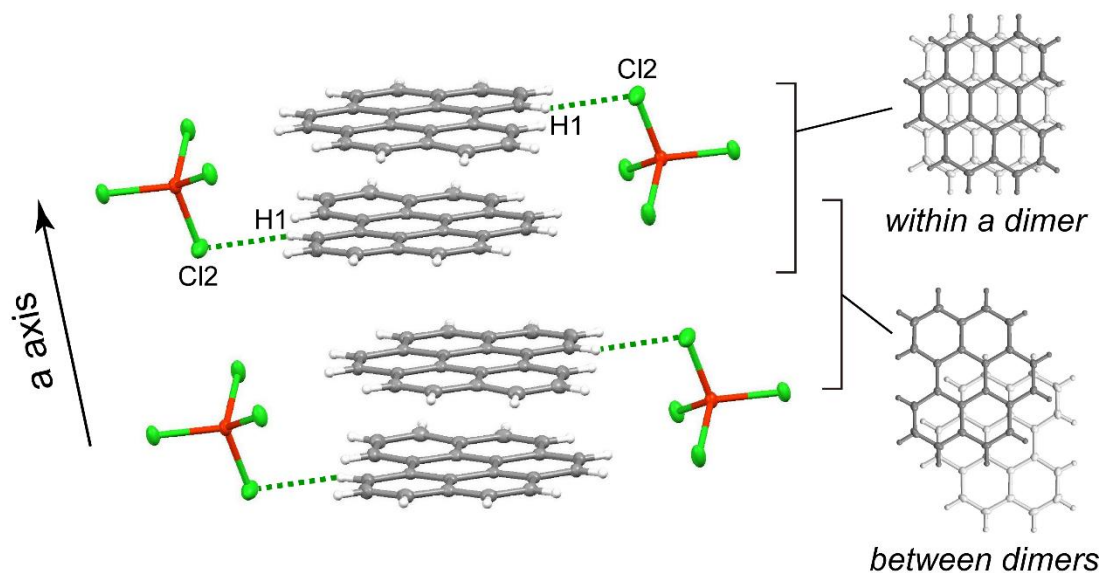


Fig. S2 Zig-zag π -stacking column of bper monocations in $(\text{bper})(\text{GaCl}_4)$, where green dotted lines show C–H \cdots Cl hydrogen bonds between bper and GaCl_4^- (H1 \cdots Cl12: 2.73 Å vs. sum of van der Waals radii: 2.95 Å²). Neighboring bper molecules within the column have a ring-over-bond overlap motif within a dimer (interplanar distance: 3.20 Å) and a ring-over-atom overlap motif between dimers (interplanar distance: 3.32 Å).

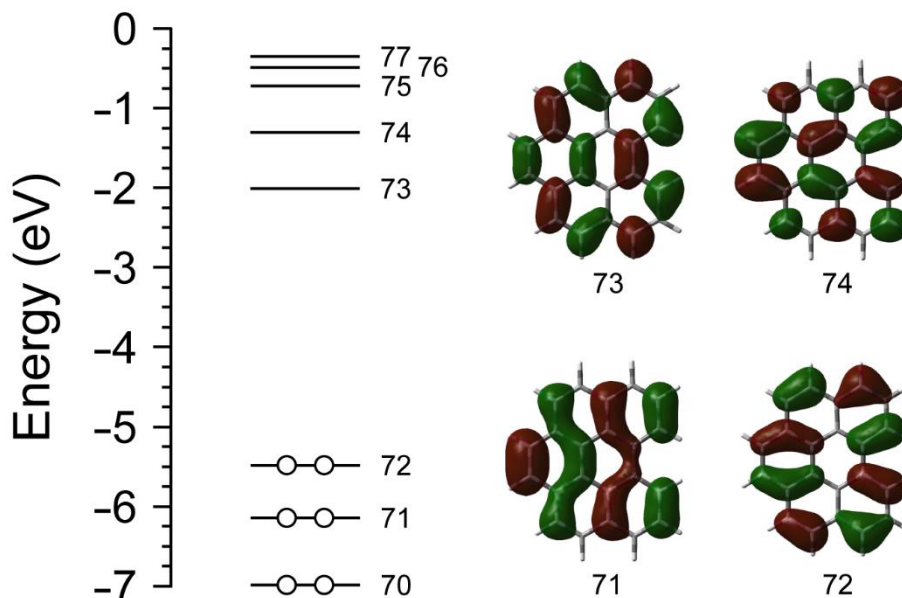


Fig. S3 Energy diagram for the frontier Kohn-Sham orbitals of the 1A_1 state in C_{2v} -symmetric neutral bper molecule calculated at the RB3LYP/6-31+G(d,p) level of theory. The 72th and 73th orbitals are the highest occupied and the lowest unoccupied orbitals, respectively. Selected orbitals are shown on the right side, where red and green surfaces are positive and negative isovalues, respectively.

References

- 1 S. Horiuchi, R. Kumai, Y. Okimoto and Y. Tokura, *Chem. Phys.*, 2006, **325**, 78.
- 2 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.