# **Supporting information**

# Understanding Single Molecule Parallel Circuits on the Basis of Frontier Orbital Theory

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#### **Resistance distance**

The resistance distance is a measure of the topological distance between two nodes in a graph.<sup>1,2</sup> When the edges of the graph with *n* nodes is replaced by unit resistors, the resistance distance between the two nodes *i* and *j*,  $(\mathbf{\Omega})_{ij}$ , is given by

$$(\mathbf{\Omega})_{ij} = (L)_{ii}^{-1} + (L)_{jj}^{-1} - 2(L)_{ij}^{-1},$$
(S1)

where *L* is the Laplacian matrix of the graph. The Laplacian matrix is defined as follows:

$$\boldsymbol{L} = \boldsymbol{D} - \boldsymbol{A},\tag{S2}$$

where  $D = diag(d_1, \dots, d_n)$  is the degree matrix and A is the adjacency matrix. The *i*th element of the degree matrix is the number of graph edges which connect the *i*th node. Let us take butadiene as an example (see Scheme 2 for the atom numbering), the adjacency matrix and the degree matrix are, respectively, given by

$$\boldsymbol{A} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \text{ and } \boldsymbol{D} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$
 (S3)

In Eq. S3, the Laplacian matrix and the inverse matrix of *L* are, respectively, given by

$$\boldsymbol{L} = \begin{pmatrix} 1 & -1 & 0 & 0\\ -1 & 2 & -1 & 0\\ 0 & -1 & 2 & -1\\ 0 & 0 & -1 & 1 \end{pmatrix}, \text{ and } \boldsymbol{L}^{-1} = \begin{pmatrix} \frac{7}{8} & \frac{1}{8} & -\frac{3}{8} & -\frac{5}{8}\\ \frac{1}{8} & \frac{3}{8} & -\frac{1}{8} & \frac{3}{8}\\ -\frac{3}{8} & -\frac{1}{8} & \frac{3}{8} & \frac{1}{8}\\ -\frac{3}{8} & -\frac{1}{8} & \frac{3}{8} & \frac{1}{8}\\ -\frac{5}{8} & -\frac{3}{8} & \frac{1}{8} & \frac{7}{8} \end{pmatrix}.$$
(S4)

Since the two electrodes connect with the 1st and 4th nodes, the resistance distance between these two nodes  $(\Omega)_{1,4}$  is calculated as  $\frac{7}{8} + \frac{7}{8} - 2\left(-\frac{5}{8}\right) = 3$ . Thus, the conductance g, which is the inverse of the resistance, is 0.333.

# Nucleus independent chemical shift

The aromaticity or anti-aromaticity of a cyclic system can be characterized by using the nucleus independent chemical shift (NICS), which is based on the calculated magnetic shielding for the ghost atom at the ring center.<sup>3–5</sup> The isotropic NICS value at the ring center is used as a quick measure for aromaticity, which is specifically called NICS(0)iso.<sup>6</sup> Since  $\pi$  MOs are expected to have a large contribution to the isotropic NICS value at 1 Å above the ring center, which is termed NICS(1)iso, this value is regarded as a better measure of  $\pi$  effects on aromaticity than NICS(0).<sup>7,8</sup> Generally, negative NICS values correspond to aromaticity, while positive values are associated with anti-aromaticity and values near zero for nonaromatics. *p*-quinodimethane has almost no aromaticity (NICS(1)iso: -1.61 ppm) whereas benzene has a strong aromaticity (NICS(1)iso: -10.2 ppm). Figure S1 shows how the NICS value varies when the model changes from biphenyl to pyrene. Here we see a small increase in aromaticity, but the variation is no more than 4 ppm. The NICS values presented here were obtained at the GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level<sup>9</sup> implemented in Gaussian 09.



**Figure S1.** NICS(1) iso values calculated on an aromatic ring of biphenyl, phenanthrene, and pyrene are shown in units of ppm. Red circles indicate the location of the ghost atom used for the NICS calculation. Note that the ghost atom is located at 1 Å above the ring center.

#### **Contribution from the cross term of Eq. (2)**

The conductance for single-molecule parallel circuits includes the cross term due to interference. In this section, we show how one can separate it from the whole transmission probability. Given  $g_1 = g_2$  in Eq. (2), the contribution from the cross term is  $2g_1$ , which is expected to be equal to  $T_{\text{parallel}}(E_{\text{F}}) - 2T_{\text{single}}(E_{\text{F}})$ , where  $T_{\text{parallel}}(E_{\text{F}})$  is the Fermi-level transmission probability for the whole parallel-path system and  $T_{\text{single}}(E_{\text{F}})$ is that for its single-path analogue. The thus-obtained contribution from the cross term is shown in Table S1.

NEGF-HMO NEGF-DFT molecule  $T(E_{\rm F})$ cross term  $T(E_{\rm F})$ cross term

 $3.34 \times 10^{-2}$ 

 $-3.08 \times 10^{-2}$ 

 $6.86 \times 10^{-2}$ 

 $1.76 \times 10^{-2}$ 

 $4.44 \times 10^{-3}$ 

 $1.76 \times 10^{-2}$ 

*p*-quinodimethane

hexatriene

benzene

butadiene

 $2.63 \times 10^{-1}$ 

 $6.96 \times 10^{-2}$ 

 $8.32 \times 10^{-2}$ 

 $1.31 \times 10^{-1}$ 

 $1.24 \times 10^{-1}$ 

 $-1.79 \times 10^{-1}$ 

Table S1. Transmission probability at the Fermi level and the contribution from the cross
term. Note that the sign of the cross term clearly shows whether the interference is in a
constructive manner or in a destructive manner.

# Verification of the validity of Eq. (6)

In this section, we verify that the zeroth order Green's function, i.e., Eq. (5), can be approximated by Eq. (6), whose squared value can be termed  $(G_{rs}^{(0)})^2 \Big|_{HOMO-LUMO}$ . In this calculation, the Hückel model was used and the imaginary infinitesimal was omitted. In Table S2, the ratio of the transmission probability at the Fermi level for the double-path system to that for the single-path system calculated with the Hückel model including all the  $\pi$  orbitals is compared with that estimated from the approximation of Eq. (6). One can see that there is a good qualitative agreement in the ratio between the two methods, justifying the use of the contributions only from the HOMO and LUMO for a quick measure of transmission.

**Table S2.** The values of  $(G_{rs}^{(0)})^2 \Big|_{HOMO-LUMO}$  calculated for *p*-quinodimethane, hexatriene, benzene, and butadiene. The ratios between the transmission probabilities at the Fermi level for the double-path system and the single-path system estimated from two methods: one is based on  $(G_{rs}^{(0)})^2 \Big|_{HOMO-LUMO}$  (third column), while the other one is based on the Hückel model including the all orbitals (fourth column).

molecule	$\left(G_{rs}^{(0)}\right)^2\Big _{\text{HOMO-LUMO}}$	double path/single path <sup>a)</sup>	$T_{\rm double}(E_{\rm F})/$ $T_{\rm single}(E_{\rm F})^{\rm b}$
p-quinodimethane	4.563	3.06	3 00
hexatriene	1.489	5.00	5.20
benzene	0.4444	0.32	0.25
butadiene	1.371	0.52	0.25

<sup>a)</sup> The ratio of the value of  $(G_{rs}^{(0)})^2 \Big|_{HOMO-LUMO}$  for the double-path system to that for

the single-path system.

<sup>b)</sup> The ratio of the transmission probability at the Fermi level for the double-path system to that for the single-path system calculated with the Hückel model including all the  $\pi$  orbitals.

Squares of molecular orbital coefficients for atoms connected to electrodes depending on  $\beta$ '



**Figure S2.** The square of molecular orbital coefficients for the atom connected with the electrode depending on  $\beta$ '.  $\beta$ ' denotes the resonance integral for the bonds highlighted by red color. In the two systems, the absolute values of the HOMO and LUMO coefficients are equal because the molecules considered here are alternant hydrocarbons. On top of that, the two electrode attachment sites are symmetrically identical. Therefore, it is only necessary to square one of the orbital coefficients of one molecular orbital.

#### Frontier orbital analysis for biphenyl-phenanthrene-pyrene system

To analyze the change in orbital energies, the absolute value of the Hückel Hamiltonian elements was continuously changed to simulate a transition from biphenyl to phenanthrene in the same way as has been done for the hexatriene-*p*-quinodimethane and butadiene-benzene systems in Figure 3. Figure S3a shows the bonds whose resonance integral,  $\beta'$ , is changed, and these bonds are highlighted in red. Figure S3b shows how the orbital energies of the whole system change as  $\beta$ 'varies. One can observe the intrusion of the second HOMO and the second LUMO into the HOMO-LUMO gap of the parent biphenyl molecule as the transition to phenanthrene goes on. Figure S3c shows the frontier orbitals of phenanthrene, where the HOMO-1 and LUMO+1 originate from the HOMO and LUMO of biphenyl, respectively. The MO amplitudes of the electrodeconnection sites in the HOMO and LUMO of phenanthrene are very small yet not zero. Their signs are hard to see, so we schematically show them using  $\oplus$  and  $\Theta$ . The product of the MO coefficients of the connection sites in the HOMO ( $C_{r,HOMO}C_{s,HOMO}$ ) is opposite in sign to that of the HOMO-1. The contribution of the HOMO-1 to the zeroth Green's function is weakened. The same is true for the pair of the LUMO and LUMO+1. The contribution of the LUMO+1 to the zeroth Green's function is weakened by the LUMO. The extent to which they are weakened is small due to the tiny amplitudes of the MO coefficients at the corresponding sites. This may be a possible reasoning, from the orbital perspective, why one can observe a tiny reduction of transmission in Figure 6a when moving from biphenyl to pyrene through phenanthrene.



**Figure S3.** (a) Kekulè structure of phenanthrene.  $\beta$ ' denotes the resonance integral for the bonds highlighted in red. (b) The orbital energy levels for phenanthrene plotted as a function of  $\beta$ '. (c) Frontier orbitals for phenanthrene ( $\beta'/\beta = 1.0$ ). Arrows in the HOMO and the LUMO show the sign of the indicated orbital coefficients.

# Local transmission contributions for the hexatriene-*p*-quinodimethane and butadiene-benzene systems



**Figure S4.** Local transmission contributions for (a) *p*-quinodimethane and (b) hexatriene at the Fermi level.



Figure S5. Local transmission contributions for (a) benzene and (b) butadiene at the Fermi level.

#### Analysis of transmission through anti-aromatic systems

In this study, decreases in conductance have been consistently associated with aromaticity. Thus, it is natural to question whether a transmission change would occur if an anti-aromatic compound is generated upon the parallelization of a molecular graph circuit. To assess this possibility, we considered the allyl radical, for which the parallel circuit analogue is cyclobutadiene, a typical anti-aromatic molecule (see Scheme S1). Although these molecules are, in reality, unstable, this was a useful thought experiment.



**Scheme S1.** Kekulé structures of the allyl radical and cyclobutadiene. Arrows show the connection points with the electrodes.

Figure S6 provides the transmission spectra for cyclobutadiene and the allyl radical, which have two and one non-bonding MOs (NBMOs) at the Fermi level, respectively. Since  $E_{\rm F} - \epsilon_{\rm k}$  becomes zero in the denominator of Eq. (5), the singularity is observed at  $E = E_{\rm F}$ . Thus, the electron transmission probability for both these compounds at the Fermi level will be as high as 1.<sup>10</sup>



**Figure S6.** Transmission spectra for cyclobutadiene (blue line) and the allyl radical (orange line) calculated using the NEGF–HMO method.

It is known that anti-aromatic molecules such as cyclobutadiene exhibit high conductivity.<sup>11,12</sup> Here, we consider the more general case of [4n] annulene, a series of anti-aromatics (see Scheme S2 for the graph theory representation). In this model, the filled nodes are connected to electrodes such that there are two paths between the two nodes and one can generate a single path subgraph terminated by the two filled nodes. The number of nodes or carbon atoms in this chain is denoted as  $m_1$ , while that in the other subgraph is  $m_2$ , and the relationship between  $m_1$  and  $m_2$  is clear:  $m_2 = m_1 - 2$ . The longer and shorter subgraphs represent linear  $C_{m_1}$  and  $C_{m_2}$  chains, respectively. Since the total number of nodes in the ring is 4n, it is evident that  $m_1 = 2n + 1$  and  $m_2 = 2n - 1$ , where  $m_1$  and  $m_2$  are odd numbers. When the number of nodes in the linear chain is odd, the linear chain has an NBMO at the Fermi level because of the Coulson-Rushbrooke pairing theorem.<sup>13</sup> Consequently, both the shorter and longer linear chains

have an NBMO at the Fermi level.

The MO diagrams for such  $\pi$ -conjugated linear carbon chains are shown in Figure S7. In this figure, moving from the lowest MO level to the highest, it is apparent that the symmetry alternates between S and A and that the *k*th MO will have A symmetry if *k* is an even number and otherwise will have S symmetry. Because the  $\frac{1}{2}(m + 1)$ th orbital corresponds to the NBMO, the *n*th and (*n*+1)th orbitals are the NBMOs in the  $C_{m_2}$  and  $C_{m_1}$  chains, respectively. If *n* is even, the NBMOs for the  $C_{m_2}$  and  $C_{m_1}$  chains will have A and S symmetry, respectively; otherwise, the symmetry is switched. What is important is that these chains do not share the same symmetry and so cannot interact with one another upon ring formation. The NBMO levels remain at the Fermi level whether the molecule is linear or cyclic, resulting in a singularity in the transmission spectrum at the Fermi level regardless of the number of paths available between the two connection nodes. Thus, the transmission probability remains unity before and after the parallelization.



Scheme S2. Molecular graph for an anti-aromatic ring and its two fragments.  $m_1$  and  $m_2$  represent the number of nodes in each fragment. Filled nodes denote locations at

which the electrode is attached.



**Figure S7.** MO level diagram for  $\pi$ -conjugated molecules with odd numbers of carbon atoms.

Atom	Coordinates (Angstroms)		
	Х	Y	Z
С	-1.172768	-0.780262	-0.000009
С	-1.275306	0.663576	-0.000017
С	0.029849	-1.401699	-0.000010
С	1.275136	-0.663148	-0.000019
2	2.478804	-1.329678	-0.000017
2	1.172581	0.780669	-0.000027
Η	0.079964	-2.485877	-0.000005
Η	-2.087768	-1.361276	-0.000004
C	-2.478992	1.330080	-0.000017
	-0.030044	1.402113	-0.000026
	-3.748098	0.737951	-0.000005
	-4.874189	0.277772	0.000004
2	3.747911	-0.737549	-0.000005
2	4.874089	-0.277580	-0.000004
•	-6.368574	-0.509837	0.000034
5	6.369015	0.509001	0.000056
Η	2.464828	-2.416588	-0.000014
Н	-2.465047	2.416991	-0.000024
ł	7.147780	-0.597940	-0.000339
ł	-7.148063	0.596594	-0.000079
Ŧ	-0.080149	2.486288	-0.000035
Ŧ	2.087564	1.361710	-0.000036

# Cartesian coordinates for the structures used for the DFT calculations

**Table S3.** Cartesian coordinates of *p*-quinodimethane in stationary point.

Atom	Coordinates (Angstroms)		
	Х	Y	Ζ
С	-1.067433	-0.452777	0.000170
С	-1.307826	0.964507	0.000145
С	0.144855	-1.071515	0.000151
С	1.438479	-0.444830	0.000084
С	2.598732	-1.148738	0.000017
Н	1.496347	0.638649	0.000089
Н	0.147717	-2.158905	0.000179
Н	-1.950021	-1.085611	0.000210
С	-2.536528	1.545602	0.000063
Н	-0.454193	1.633343	0.000209
С	-3.774641	0.872157	-0.000015
С	-4.870161	0.348498	-0.000065
С	3.888325	-0.585375	-0.000021
С	5.023380	-0.153558	-0.000054
S	-6.316165	-0.528096	-0.000111
S	6.531537	0.610220	-0.000061
Н	2.556386	-2.236343	0.000008
Н	-2.597349	2.630400	0.000068
Н	7.292003	-0.509268	-0.000594
Н	-7.159944	0.529924	-0.000274

 Table S4. Cartesian coordinates of hexatriene in stationary point.

Atom	Coordinates (Angstroms)		
	Х	Y	Ζ
C	-0 692766	-1 195909	0.003629
C C	-1.413174	0.013167	0.001684
C	0.692845	-1.195865	-0.003556
С	1.413181	0.013246	-0.001565
С	2.834388	0.012556	-0.002032
С	0.692704	1.222322	0.002767
Н	1.232866	-2.134852	-0.007758
Н	-1.232765	-2.134906	0.007902
С	-2.834378	0.012315	0.002075
С	-0.692781	1.222308	-0.002574
С	-4.045830	0.026835	0.012600
S	-5.734127	-0.103826	-0.027780
С	4.045836	0.027087	-0.012725
S	5.734107	-0.103885	0.027742
Н	-6.012355	1.161409	0.362427
Н	6.012566	1.160675	-0.364479
Н	-1.232827	2.161309	-0.006030
Н	1.232666	2.161377	0.006736

 Table S5. Cartesian coordinates of benzene in stationary point.

Atom	Coordinates (Angstroms)			
	Х	Y	Z	
				<u> </u>
С	-0.724061	0.885974	0.005273	
С	-1.525646	-0.193452	-0.165479	
С	0.724052	0.885982	-0.005279	
С	1.525648	-0.193435	0.165473	
С	2.931645	-0.165885	0.098436	
Н	1.084581	-1.165024	0.377284	
Н	1.198523	1.852104	-0.149866	
Н	-1.198543	1.852092	0.149857	
С	-2.931644	-0.165917	-0.098444	
Н	-1.084570	-1.165036	-0.377290	
С	-4.144913	-0.199352	-0.058368	
S	-5.825412	-0.086891	0.086463	
С	4.144914	-0.199336	0.058366	
S	5.825416	-0.086901	-0.086454	
Н	-6.131017	-1.260460	-0.514433	
Н	6.131001	-1.260477	0.514439	

 Table S6. Cartesian coordinates of butadiene in stationary point.

Atom	Coordinates (Angstroms)			
	Х	Y	Ζ	
C	-0.000065	0.743616	0.000000	
С	1.196027	1.484581	-0.000000	
С	1.202940	2.870950	0.000000	
С	-0.000065	3.597373	0.000000	
С	-1.203149	2.871054	0.000000	
С	-1.196114	1.484624	0.000000	
Н	2.152632	0.979572	-0.000000	
Н	2.146033	3.404121	0.000000	
С	-0.001186	5.018269	0.000000	
Н	-2.146076	3.404482	0.000000	
Н	-2.152783	0.979748	0.000000	
С	0.000065	-0.743616	0.000000	
С	-1.196027	-1.484581	-0.000000	
С	-1.202940	-2.870950	-0.000000	
С	0.000065	-3.597373	0.000000	
С	1.203149	-2.871054	0.000000	
С	1.196114	-1.484624	0.000000	
Н	-2.152632	-0.979572	-0.000000	
Н	-2.146033	-3.404121	-0.000000	
С	0.001186	-5.018269	0.000000	
Н	2.146076	-3.404482	0.000000	
Н	2.152783	-0.979748	0.000000	
С	-0.013980	-6.229722	-0.000000	
S	0.118943	-7.918302	-0.000000	
Н	-1.205872	-8.192595	-0.000000	
С	0.013980	6.229722	-0.000000	
S	-0.118943	7.918302	-0.000000	
Н	1.205872	8.192595	-0.000000	

 Table S7. Cartesian coordinates of biphenyl in stationary point.

Atom	Coordinates (Angstroms)		
	Х	Y	Z
	0.520775	0.570107	0.00000
C	0.552775	0.370107	0.000000
C	1.91/986	0.855968	0.000000
С	2.392481	2.147684	0.000000
С	1.498004	3.248616	0.000000
С	0.131573	2.990458	-0.000000
С	-0.368249	1.673823	-0.000000
Н	2.637398	0.047416	0.000000
Н	3.459357	2.334694	0.000000
С	1.996638	4.580291	0.000000
Н	-0.568753	3.817873	-0.000000
С	0.000000	-0.780018	0.000000
С	-1.411875	-0.971143	-0.000000
С	-1.945872	-2.274241	-0.000000
С	-1.124054	-3.395979	-0.000000
С	0.281182	-3.202523	0.000000
С	0.816598	-1.934753	0.000000
С	-2.281131	0.170996	-0.000000
Н	-3.022579	-2.399945	-0.000000
С	-1.667358	-4.710088	-0.000000
Н	0.932617	-4.067875	0.000000
Н	1.894301	-1.835620	0.000000
С	-2.134475	-5.827691	-0.000000
S	-2.645960	-7.442559	-0.000000
Н	-3.976621	-7.199345	-0.000000
С	2.445767	5.705300	0.000000
S	2.921625	7.331062	0.000000

**Table S8.** Cartesian coordinates of phenanthrene in stationary point.

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Н	4.257265	7.116965	0.000000
С	-1.783221	1.433046	-0.000000
Н	-3.352850	0.003004	-0.000000
Н	-2.451380	2.287668	-0.000000

 Table S9. Cartesian coordinates of pyrene in stationary point.

Atom	Coordinates (Angstroms)		
	Х	Y	Ζ
C	0.000000	-0.710824	0.000000
С	1.232710	-1.427913	0.000000
С	1.212595	-2.825502	0.000000
С	0.000038	-3.533727	0.000000
С	-1.212777	-2.825482	0.000000
С	-1.232847	-1.427811	0.000000
Н	2.147666	-3.373531	0.000000
С	-0.000667	-4.957402	0.000000
Н	-2.147477	-3.374097	0.000000
С	0.000098	0.710903	-0.000000
С	-1.232711	1.427988	-0.000000
С	-1.212519	2.825542	-0.000000
С	0.000212	3.533723	-0.000000
С	1.212885	2.825415	-0.000000
С	1.232810	1.427732	-0.000000
С	-2.460765	0.679408	0.000000
Н	-2.147477	3.373763	-0.000000
С	0.000792	4.957364	-0.000000
Н	2.147754	3.373791	-0.000000
С	-0.015685	6.168318	-0.000000
S	0.117701	7.857365	-0.000000
Н	-1.206848	8.132211	-0.000000

С	0.015585	-6.168354	0.000000
S	-0.117815	-7.857394	0.000000
Н	1.206747	-8.132177	0.000000
С	-2.460933	-0.679146	0.000000
Н	-3.397629	1.226444	0.000000
Н	-3.397834	-1.226112	0.000000
С	2.460806	0.679234	-0.000000
С	2.460630	-0.679386	-0.000000
Н	3.397860	1.226016	-0.000000
Н	3.397522	-1.226325	-0.000000

# References

- Klein, D. J.; Randić, M. Resistance Distance. J. Math. Chem. 1993, 12 (1), 81–95.
   https://doi.org/10.1007/BF01164627.
- Babić, D.; Klein, D. J.; Lukovits, I.; Nikolić, S.; Trinajstić, N. Resistance-Distance Matrix: A Computational Algorithm and Its Application. *Int. J. Quantum Chem.* 2002, *90* (1), 166–176. https://doi.org/10.1002/qua.10057.
- (3) Schleyer, P. von R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Van Eikema Hommes, N. J. R. Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. J. Am. Chem. Soc. 1996, 118 (26), 6317–6318. https://doi.org/10.1021/ja960582d.
- Jiao, H.; Von Ragué Schleyer, P.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. Magnetic Evidence for the Aromaticity and Antiaromaticity of Charged Fluorenyl, Indenyl, and Cyclopentadienyl Systems. *J. Am. Chem. Soc.* 1997, *119* (30), 7075–7083. https://doi.org/10.1021/ja970380x.
- (5) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; v. R. Schleyer, P. NICS as an Aromaticity Criterion. *Chem. Rev.* 2005, 105, 3842. https://doi.org/10.1021/cr030088.
- (6) Von Ragué Schleyer, P.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta,
   R.; Van Eikema Hommes, N. J. R. Dissected Nucleus-Independent Chemical Shift
   Analysis of π-Aromaticity and Antiaromaticity. *Org. Lett.* 2001, *3* (16), 2465–2468.
   https://doi.org/10.1021/ol016217v.
- (7) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.;

Schleyer, P. V. R. Which NICS Aromaticity Index for Planar  $\pi$  Rings Is Best? *Org. Lett.* **2006**, *8* (5), 863–866. https://doi.org/10.1021/ol0529546.

- Cui, Y.-H.; Tian, W. Q.; Feng, J.-K.; Li, W.-Q.; Liu, Z.-Z. Aromaticity of Ni Bis-Dithiolenes Complexes. J. Mol. Struct. THEOCHEM 2009, 897 (1), 61–65. https://doi.org/https://doi.org/10.1016/j.theochem.2008.11.023.
- Wolinski, K.; Hinton, J. F.; Pulay, P. Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations. *J. Am. Chem. Soc.* 1990, *112* (23), 8251–8260. https://doi.org/10.1021/ja00179a005.
- (10) Tsuji, Y.; Staykov, A.; Yoshizawa, K. Orbital Determining Spintronic Properties of a π-Conjugated System. J. Phys. Chem. C 2012, 116 (30), 16325–16332. https://doi.org/10.1021/jp305448q.
- (11) Fujii, S.; Marqués-González, S.; Shin, J. Y.; Shinokubo, H.; Masuda, T.; Nishino, T.; Arasu, N. P.; Vázquez, H.; Kiguchi, M. Highly-Conducting Molecular Circuits Based on Antiaromaticity. *Nat. Commun.* 2017, *8.* https://doi.org/10.1038/ncomms15984.
- (12) Yin, X.; Zang, Y.; Zhu, L.; Low, J. Z.; Liu, Z. F.; Cui, J.; Neaton, J. B.; Venkataraman, L.; Campos, L. M. A Reversible Single-Molecule Switch Based on Activated Antiaromaticity. *Sci. Adv.* 2017, *3* (10). https://doi.org/10.1126/sciadv.aao2615.
- (13) Coulson, C. A.; Rushbrooke, G. S. Note on the Method of Molecular Orbitals.
   Math. Proc. Cambridge Philos. Soc. 1940, 36 (2), 193–200. https://doi.org/10.1017/S0305004100017163.