Electronic Supporting Information

The influence of nitrogen position on charge carrier mobility in enantiopure aza[6]helicene crystals

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General procedure

The charge hopping rate from molecule *i* to *k* is given by the Marcus equation:[1]

$$\Gamma_{ik} = \frac{|J_{ik}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda K_b T}}exp\left\{-\frac{(\Delta E_{ik}+\lambda)^2}{4\lambda K_b T}\right\}$$

J_{ik} is the transfer integral, ΔE_{ik} is the change in energy between molecules *i* and *k*, and λ is the reorganisation energy. The reorganisation energy is the sum of the energy cost associated with the rearrangement of the molecules involved in the hop and their surroundings, respectively called inner (λ_{in}) and outer (λ_{ou}) reorganisation energies. λ_{in} is calculated with the 4-point method:[2]

$$\lambda_{in} = (E_n^{+/-} - E_c^{+/-} + E_c^0 - E_n^0)$$

The superscript *+/-* and *0* indicate the charged and neutral systems respectively and the subscript *n* and *c* indicate that the energy is calculated at the neutral or charged molecular geometry. The outer reorganisation energy is harder to quantify, so was approximated to 0.3 eV for all the structures studied. As the maximum transfer integral found was ≈0.07 eV and λ was always higher than 0.4 eV, the assumption of weak coupling ($J \ll \lambda$) was valid. For all structures studied, the maximum transfer integral was less than 0.1 eV.

The change in energy between the sites is:

$$\boldsymbol{\Delta E_{ik}} = \boldsymbol{\varepsilon_i} - \boldsymbol{\varepsilon_k} - \mathbf{qF}\cdot\boldsymbol{r_{ik}}$$

where ε_i and ε_k are the energies of frontier orbitals for molecule *i* and *k* respectively, *q* is the charge on an electron, ***F*** is the field vector and $\boldsymbol{r}_{ik}$ is the distance vector between sites *i* and *k*. As we do not include energetic disorder in the model, $\varepsilon_i = \varepsilon_k$ and the only contribution to $\boldsymbol{\Delta E_{ik}}$ is given by the electric field. The angular dependent mobility was found with this method by applying a field of strength 10000 V cm^{-1} at 10 degrees intervals in each of the 3 planes. To obtain a mobility from the set of rates, we used a Master equation approach:[3]

$$\frac{\boldsymbol{dP_k}}{\boldsymbol{dP_i}} = \sum_{\boldsymbol{i\neq k}}[\boldsymbol{\Gamma_{ik}P_i(t)} - \boldsymbol{\Gamma_{ki}P_k(t)}]$$

P_k is the probability of site *k* being occupied by a charge and Γ_{ik} is the rate of hopping between sites *i* and *k*. The equation is valid in the low charge limit. By considering a matrix *A* defined as:

$$\boldsymbol{A_{ik}} = \begin{cases} \boldsymbol{\Gamma_{ik}, i \neq k} \\ -\sum_{\boldsymbol{i\neq k}} \boldsymbol{\Gamma_{ik}}, \boldsymbol{i = k} \end{cases}$$

The master equation can be solved in steady state with *AP = 0*. The average velocity of charges can then be found through the steady state probabilities:

$$\boldsymbol{v} = \sum_{\boldsymbol{i\neq k}} \mathbf{r}_{\boldsymbol{ik}}\boldsymbol{A_{ik}P_k}$$

The last step is to calculate the charge mobility:

$$\boldsymbol{\mu} = \frac{\overline{\boldsymbol{v}}}{\boldsymbol{F}}$$

$\overline{\boldsymbol{v}}$ is the average velocity of the charges in the direction of the field and F is the magnitude of the field.

Crystal cell similarity

	6-aza[6]helicene (**PIHDOB**)	1-aza[6]helicene (**BAGLIH**)	2-aza[6]helicene (**BAGLED**)	[6]helicene (**HEXHEL**)	Mean	Standard deviation
a (Å)	7.214	7.293	7.256	7.344	7.277	0.055
b (Å)	13.058	12.979	13.028	13.156	13.055	0.074
c (Å)	17.660	17.368	17.234	17.511	17.443	0.183

Table S1. Lengths of the (aza)[6]helicene enantiopure cells reported in the Cambridge Structural Database (CSD). Space group is always $P2_12_12_1$. Mean and standard deviation are reported to show the small differences between the crystal structures.

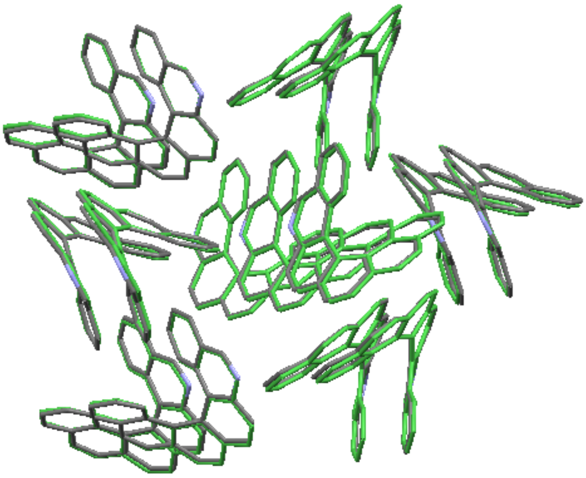


Figure S1. Overlay of HEXHEL (green) and PIHDOB (grey) crystal structures sharing the same supramolecular packing.

Geometrical Parameters

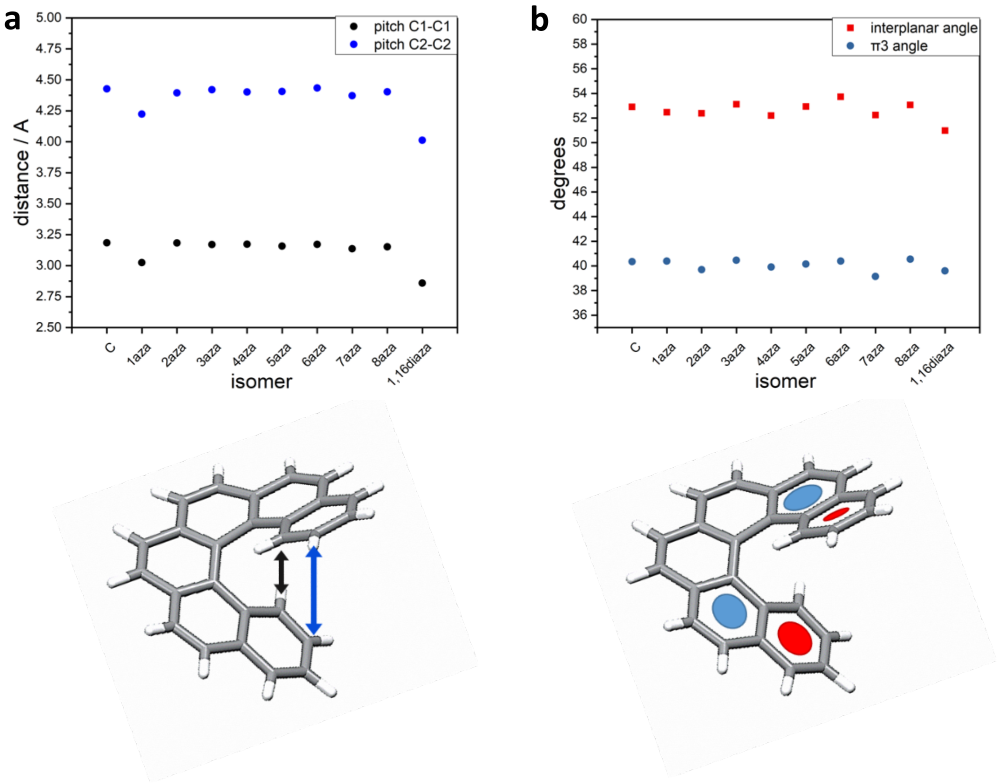


Figure S2. Plots of [6]helicenes geometrical parameters. (a) Pitch defined as distance between C1 and C16 (black dots) and distance between C2 and C15 (blue dots). (b) Interplanar angle between terminal rings (red dots) and between 2° and 5° ring (cyan dots). The variations over the series are quite small. The only exceptions occur when nitrogen is in position 1 because of the reduced steric hindrance given by the removed C-H bond(s).

Molecular Orbitals

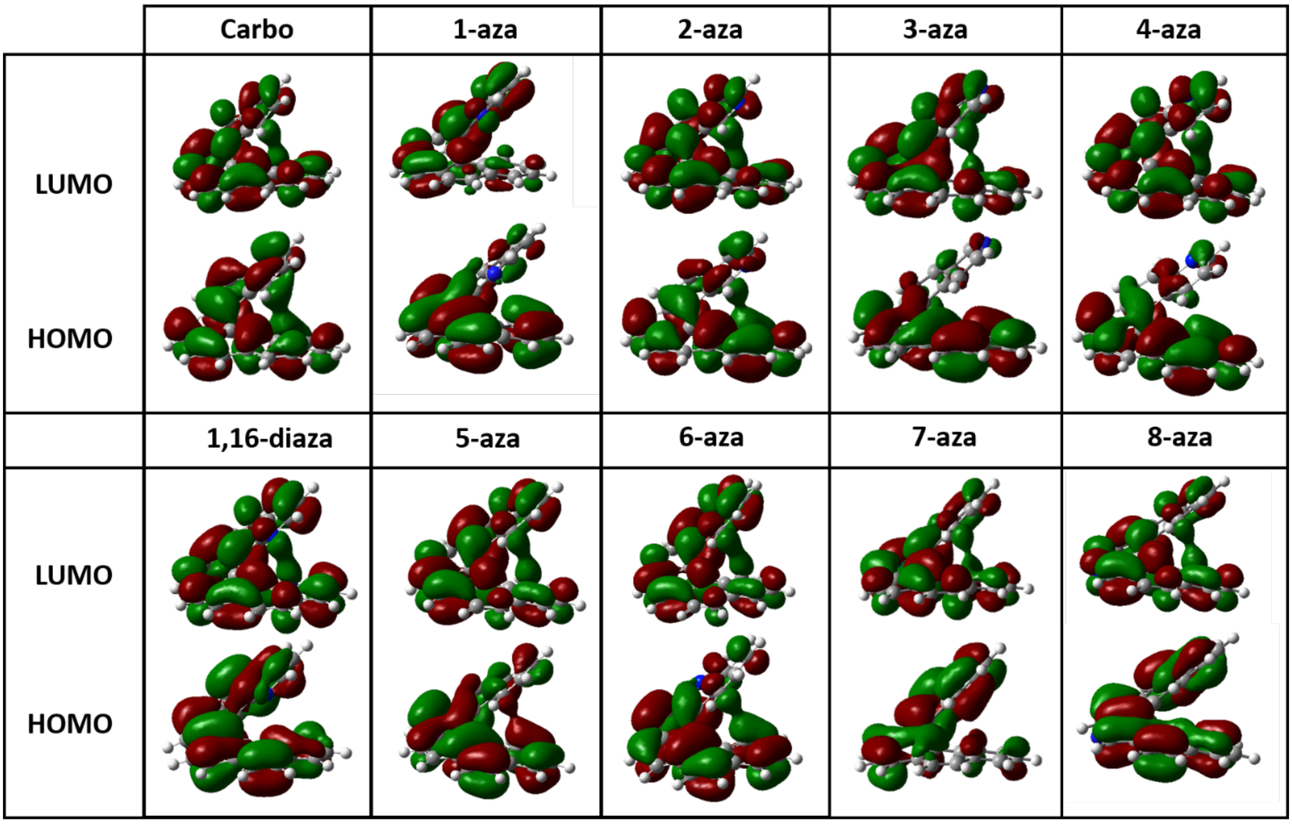


Figure S3. HOMO and LUMO orbitals for three of the isomers studied (isovalue 0.02). The HOMO is clearly localized far from the pyridinic ring in **1-aza** and close to it in **7-aza**. The opposite is true for LUMOs. In **8-aza**, there is no big change between HOMO and LUMO in terms of localization areas. the **carbo**[6]helicene and **1,16-diaza**, as they are C_2 symmetric, do not show differences between two sides of the helicene. Nitrogen atoms are shown in blue.

Additional plots

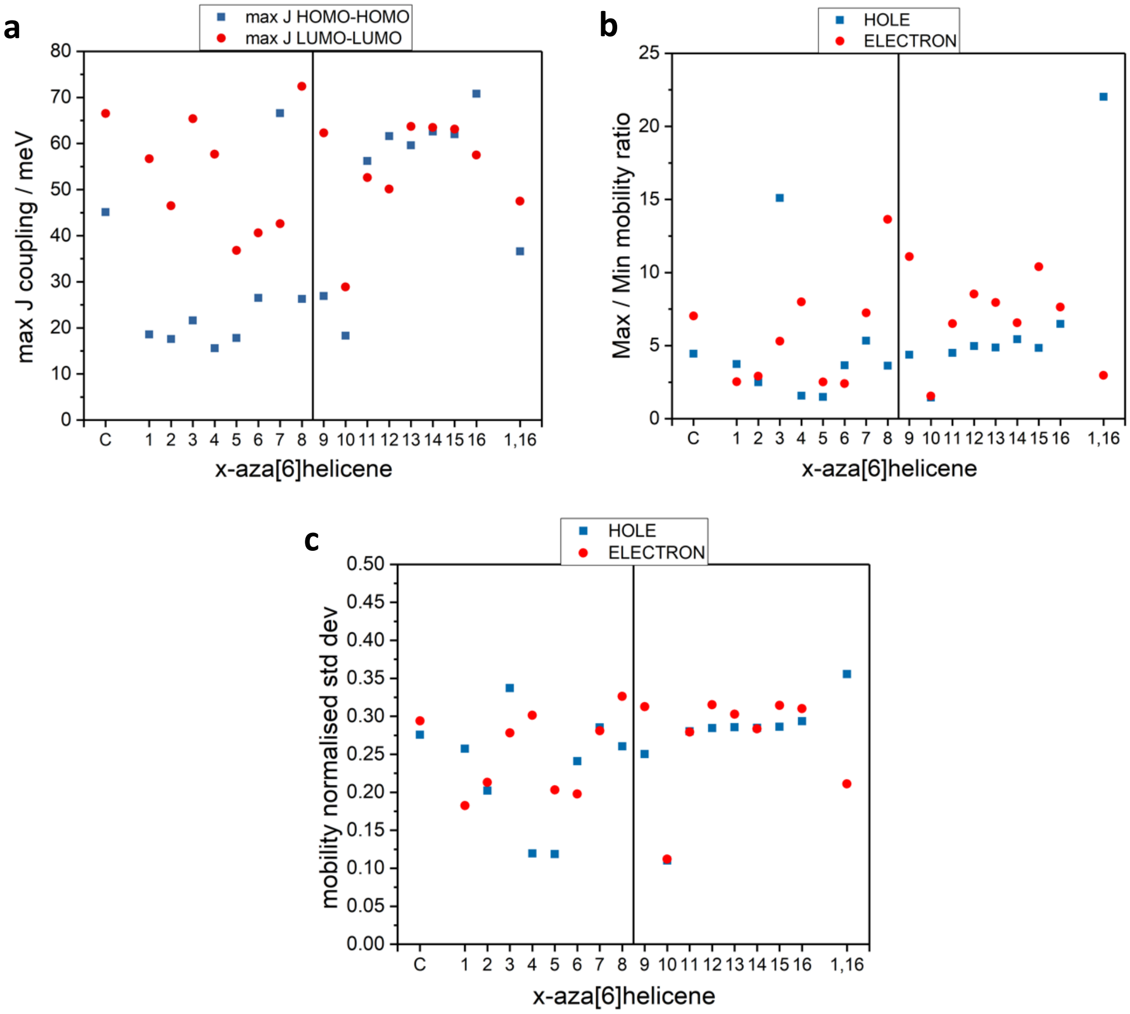


Figure S4. Calculated properties for the hypothetical aza[6]helicene cells studied. The number of the *x*-axis entries indicates the position of the nitrogen in the aza[6]helicene scaffold. The entries C and 1,16 indicate the carbo[6]helicene (no nitrogen) and the 1,16-diaza[6]helicene, respectively. (a) Maximum transfer integral (b) The ratio between the maximum and minimum mobility as an indication of anisotropy. (c) The normalised standard deviation of anisotropy (*i.e.* divided by maximum mobility) as another indication of charge carrier anisotropy.

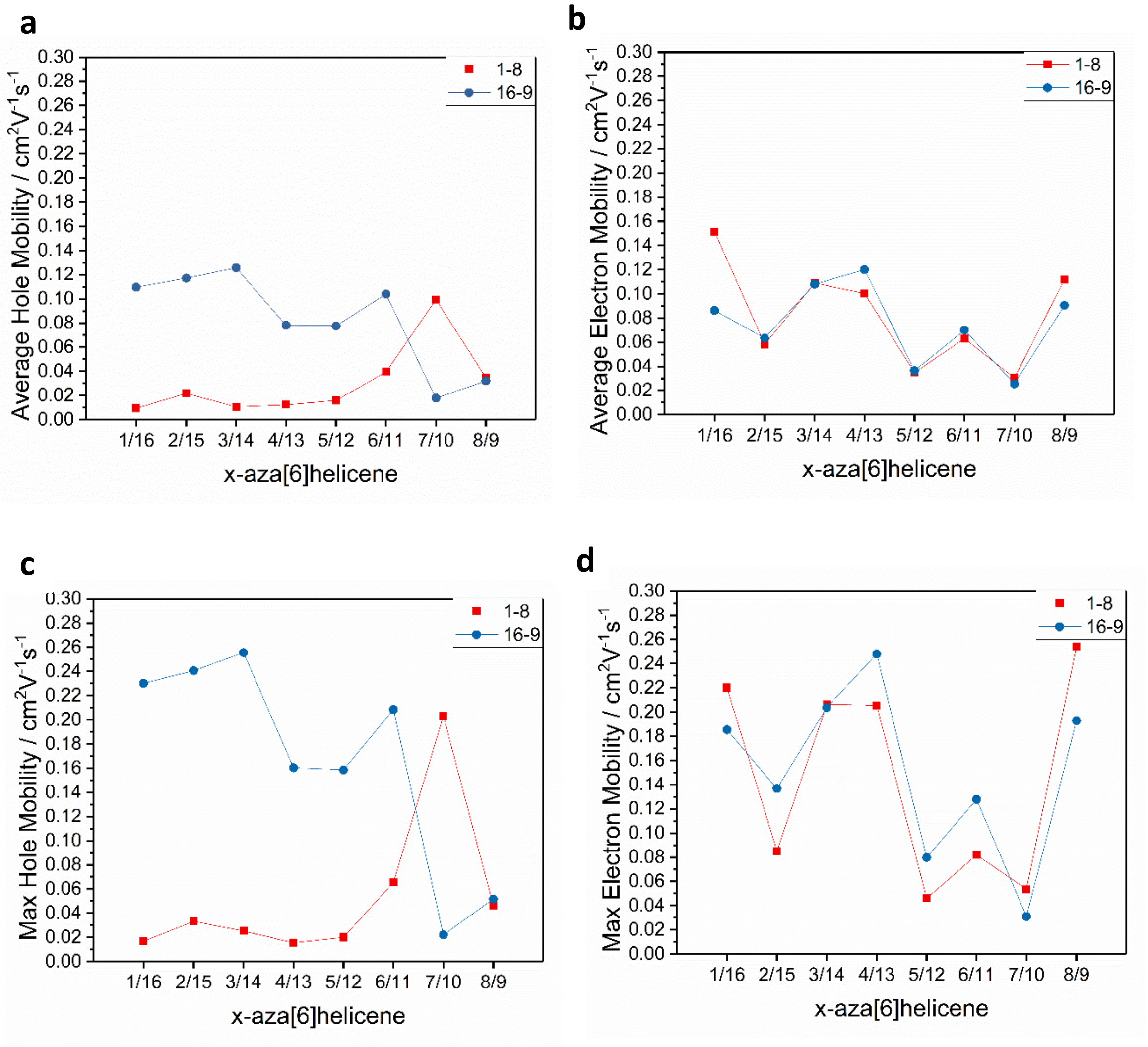


Figure S5. Average hole (a) and electron (b) mobility for cells containing helicene isomers with opposite occupancy. Maximum hole (c) and electron (d) mobility for cells containing helicene isomers with opposite occupancy.

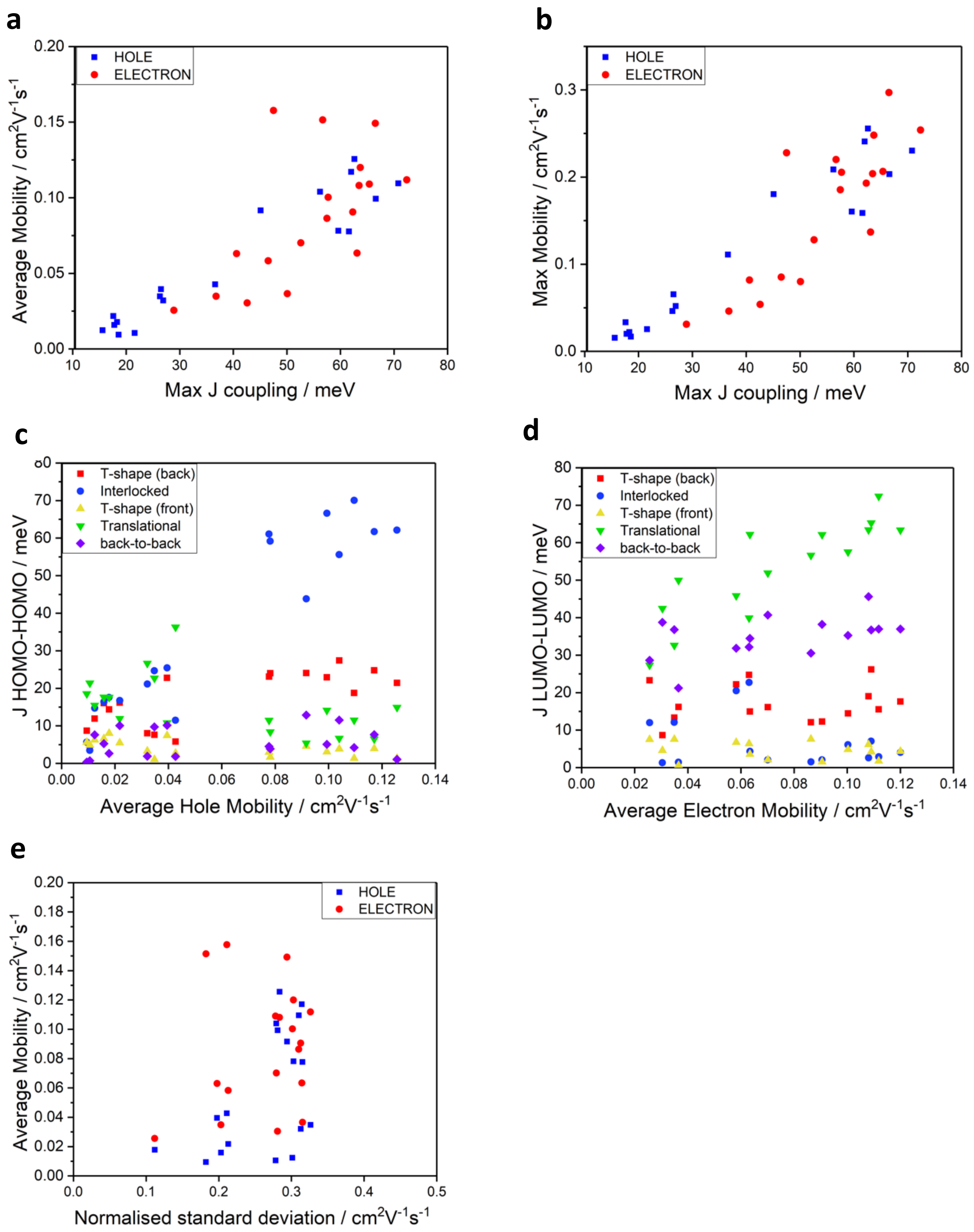


Figure S6. Max transfer integrals (J) against (a) Average mobility and (b) Maximum mobility. Average mobility against transfer integrals for each dimer motif (c,d). Normalised standard deviation against average mobility (e).

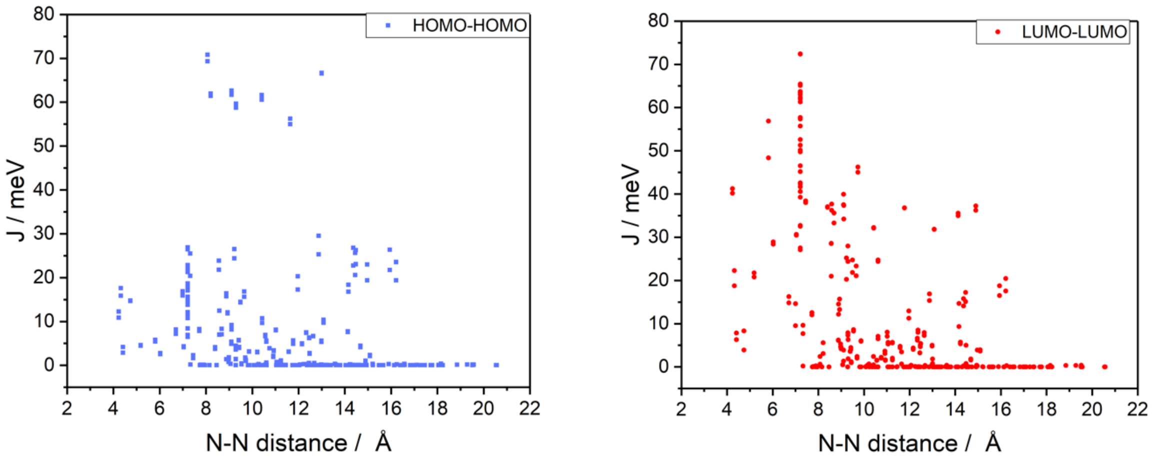


Figure S7. HOMO-HOMO and LUMO-LUMO transfer integrals for all the dimers in all the hypothetical cells studied (from **1-aza** to **16-aza**) plotted against the nitrogen-nitrogen distance.

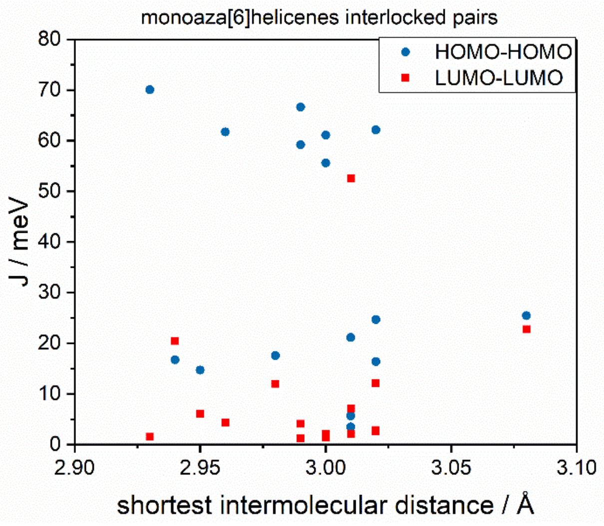


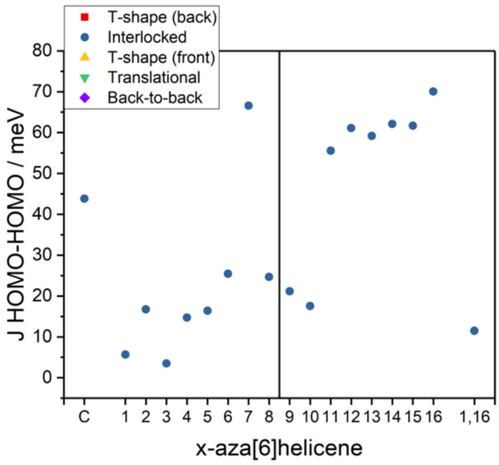
Figure S8. Transfer integral values against the shortest intermolecular distance (C···C or C···N) for the interlocked motif in all the monoaza[6]helicene crystal cells studied.

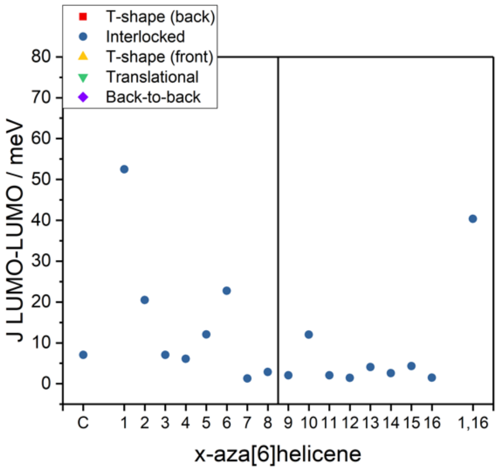
	HOLE					ELECTRON				
Aza-x isomer	**Min μ (cm^2/Vs)**	**Max μ (cm^2/Vs)**	**Average μ (cm^2/Vs)**	**Anisotropy (cm^2/Vs)**	**λ_{in} (meV)**	**Min μ (cm^2/Vs)**	**Max μ (cm^2/Vs)**	**Average μ (cm^2/Vs)**	**Anisotropy (cm^2/Vs)**	**λ_{in} (meV)**
C	0.040	0.180	0.092	0.276	159	0.042	**0.297**	0.149	0.294	160
1	**0.004**	0.017	0.010	0.257	199	**0.087**	0.220	0.151	0.182	171
2	0.013	0.033	0.022	0.202	180	0.029	0.085	0.058	0.213	217
3	0.002	0.025	**0.011**	0.337	170	0.039	0.206	0.109	0.278	189
4	0.010	**0.016**	0.012	0.119	210	0.026	0.26	0.100	0.301	167
5	0.013	0.020	0.016	0.119	**216**	0.018	0.046	0.035	0.203	224
6	0.018	0.066	0.040	0.241	182	0.034	0.081	0.063	0.198	198
7	0.038	0.203	0.099	0.285	206	**0.007**	0.054	0.030	0.281	**245**
8	0.013	0.046	0.035	0.261	159	0.019	0.254	0.112	**0.326**	187
9	0.012	0.052	0.032	0.250	159	0.017	0.193	0.091	0.313	187
10	0.015	0.022	0.018	**0.110**	206	0.020	**0.031**	**0.026**	**0.112**	**245**
11	0.046	0.209	0.104	0.280	182	0.020	0.128	0.070	0.279	198
12	0.032	0.159	0.078	0.285	**216**	0.009	0.080	0.037	0.315	224
13	0.033	0.160	0.078	0.286	210	0.031	0.248	0.120	0.302	167
14	0.047	**0.256**	**0.126**	0.285	170	0.031	0.204	0.108	0.284	189
15	**0.050**	0.241	0.117	0.286	180	0.013	0.137	0.063	0.314	217
16	0.035	0.230	0.110	0.294	199	0.024	0.185	0.086	0.310	171
1,16	0.005	0.111	0.043	**0.356**	**147**	0.077	0.228	**0.158**	0.211	**147**

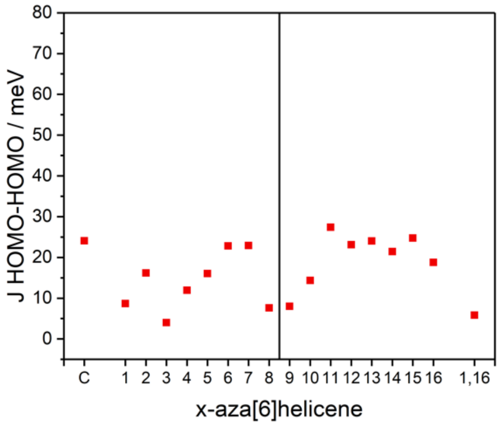
Table S2. Charge mobility related properties for the aza[6]helicenes analysed in this work. The anisotropy here is calculated as normalised standard deviation of the direction-dependent charge mobility. The best (worst) values are highlighted in green (orange), assuming the best values correspond to high mobility and low anisotropy.

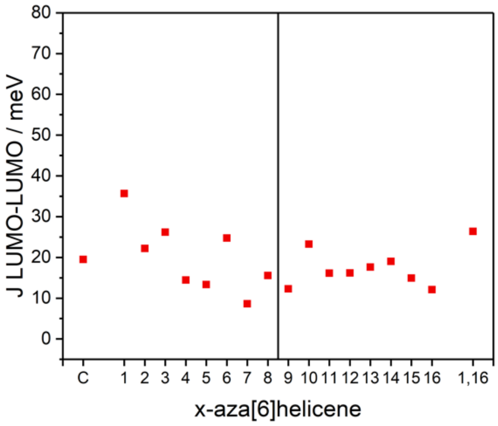
Single motif transfer integrals J for the whole series

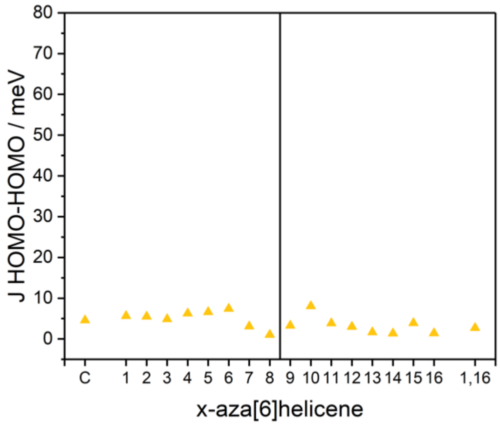
HOLE **ELECTRON**

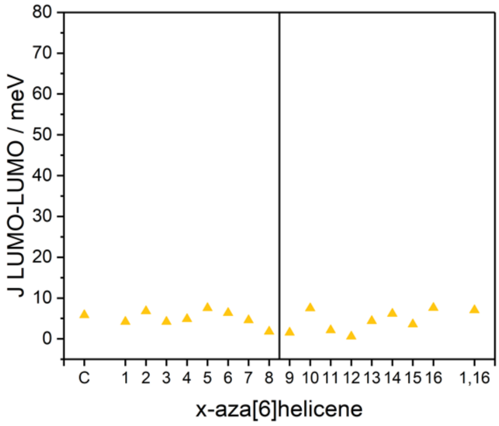


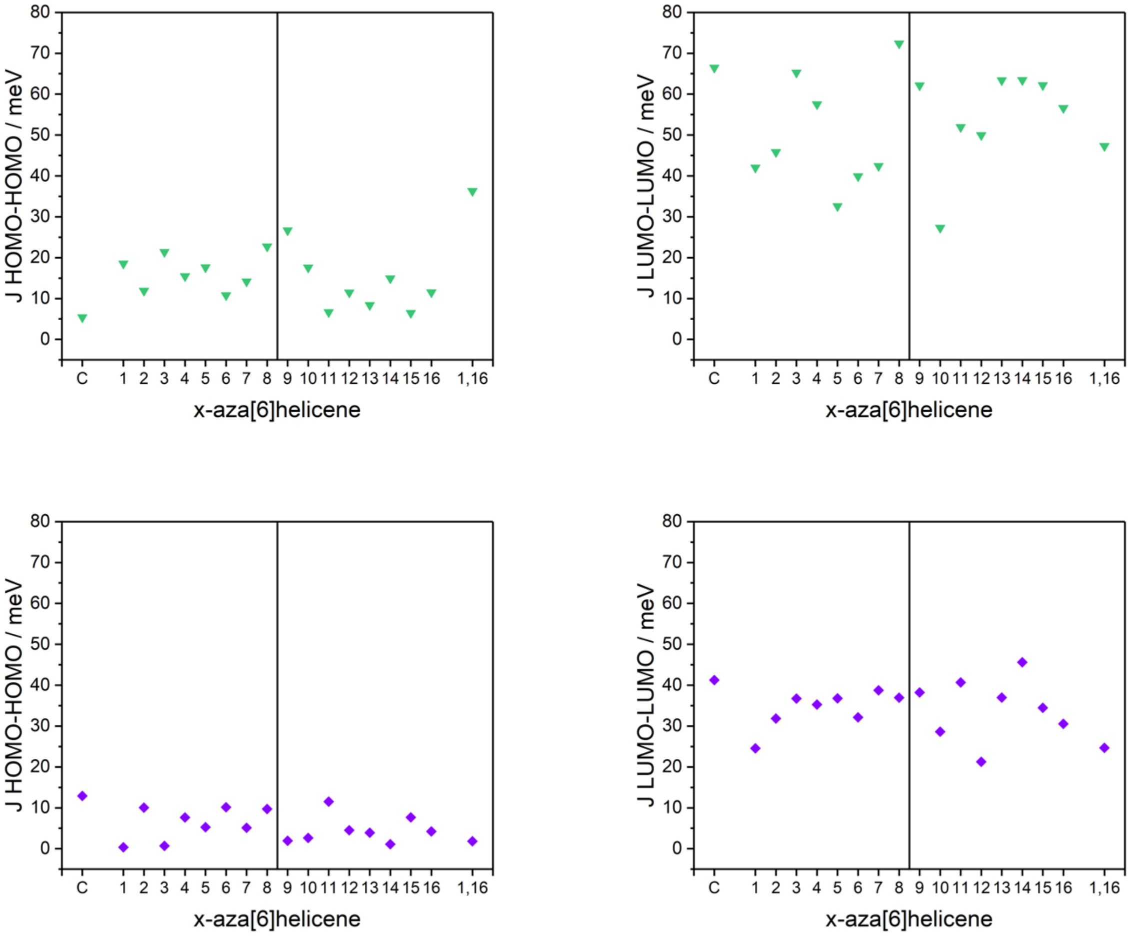












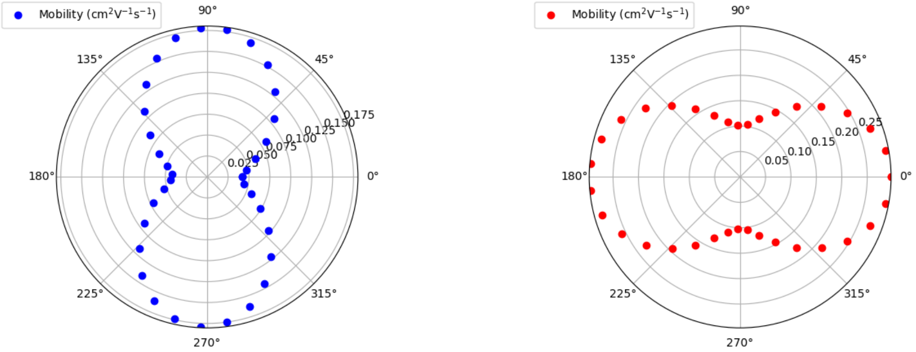
Figures S9. Transfer integrals (J) for each motif separately for the whole aza[6]helicene series studied.

Mobility angular distribution plots

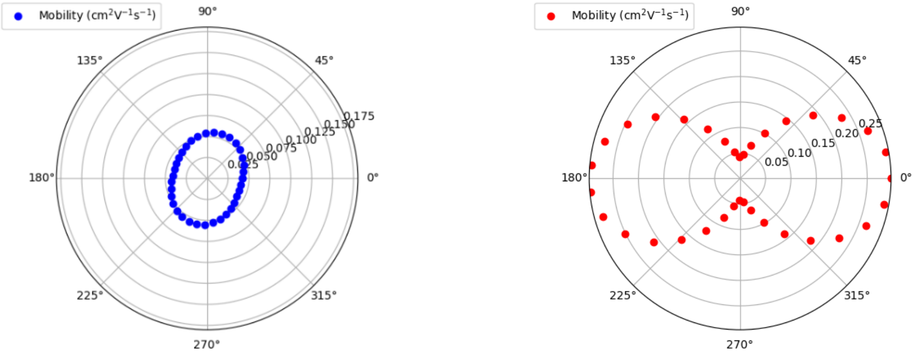
Figures S10. Angular distribution of the mobility in the three orthogonal planes for hole (**blue**) and electron (**red**) transport. Please note that the scale is set at the maximum mobility value, which is different for every isomer.

Carbo[6]helicene

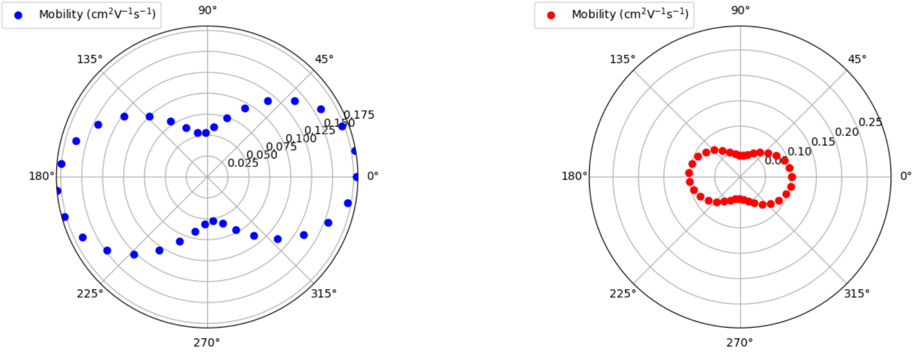
ab plane



ac plane

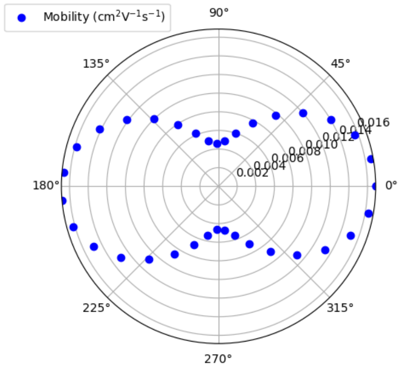


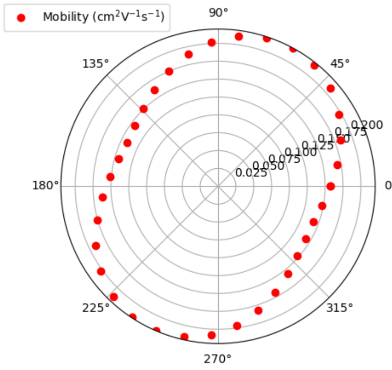
bc plane



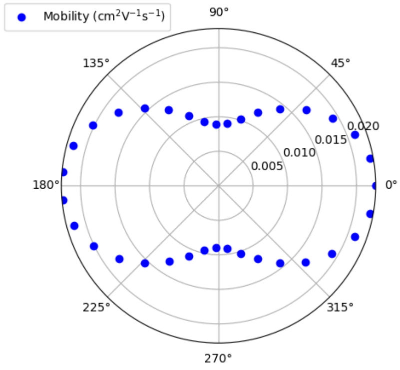
1-aza[6]helicene

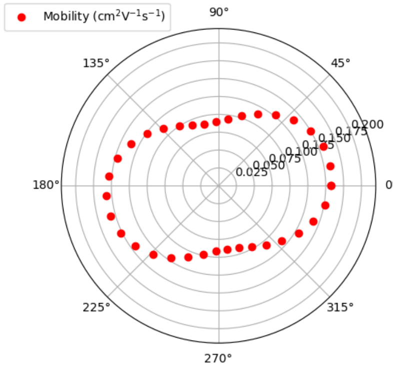
ab plane





ac plane





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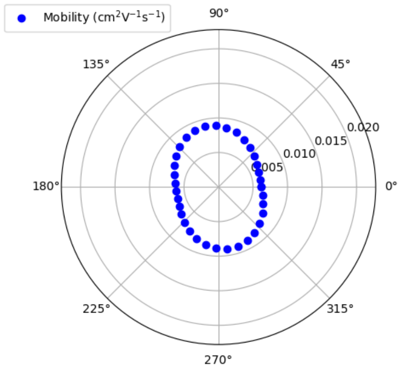
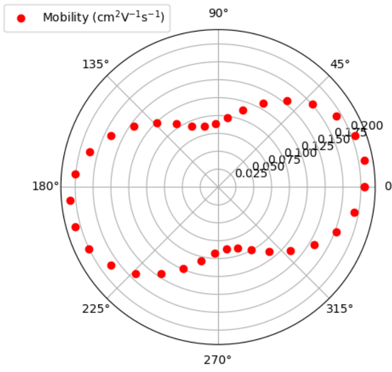
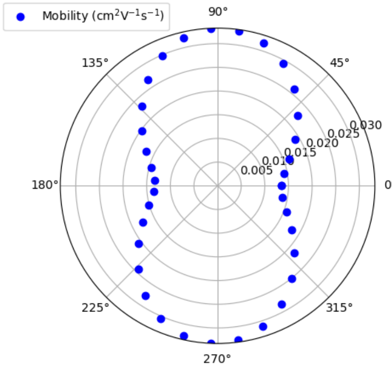
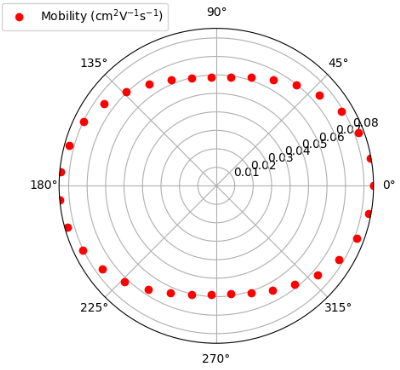




2-aza[6]helicene

ab plane





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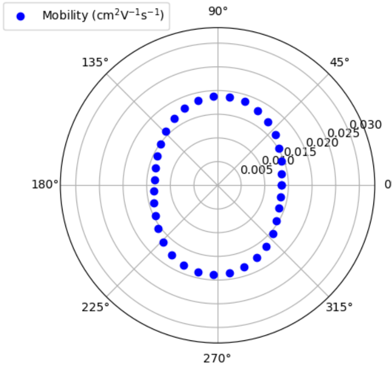

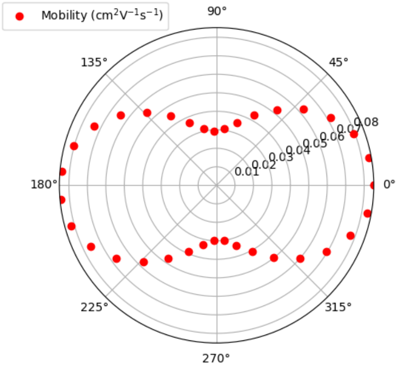

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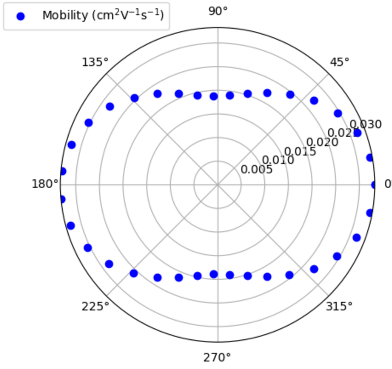
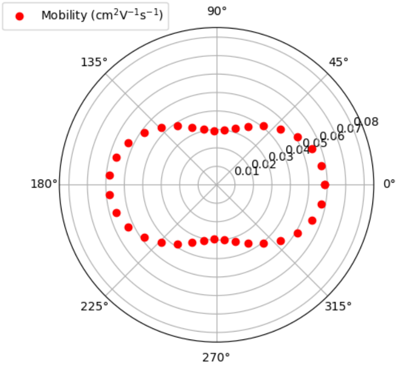
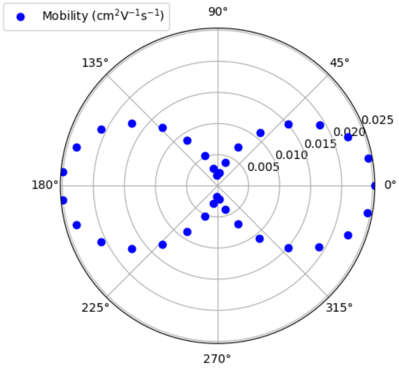
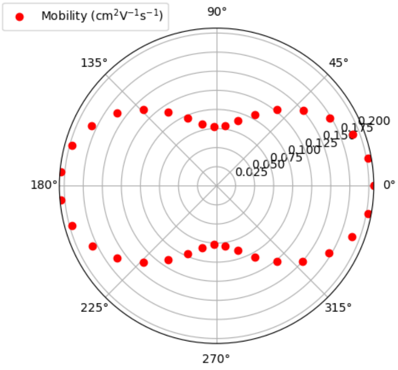




3-aza[6]helicene

ab plane





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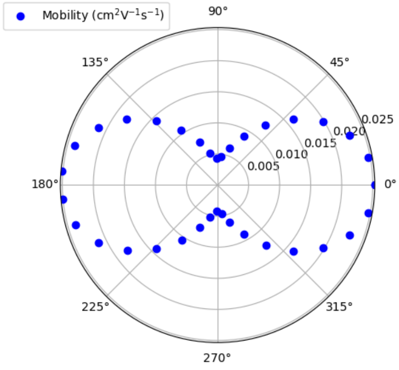

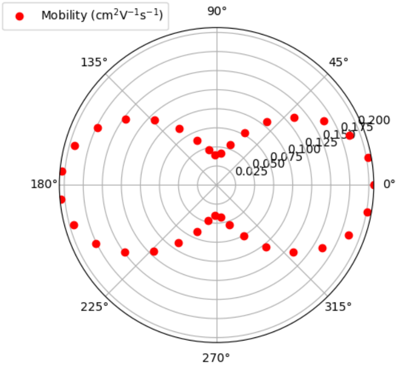

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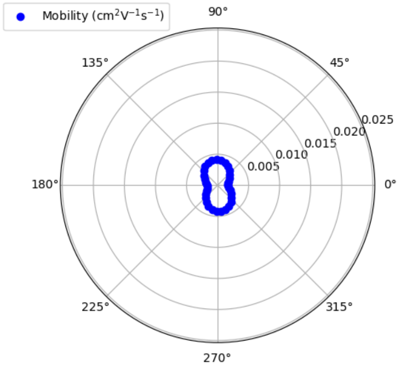
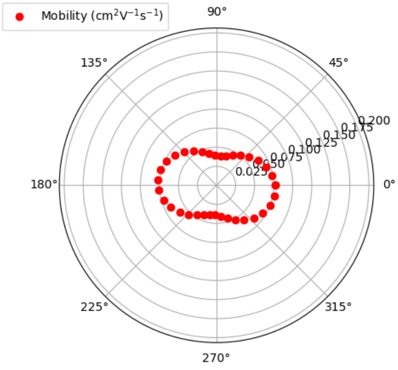
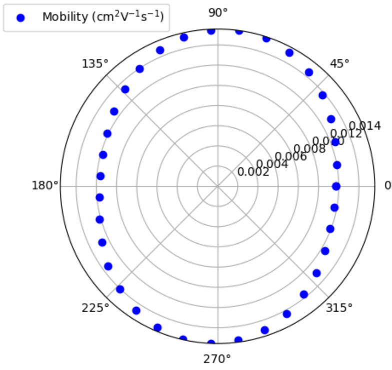
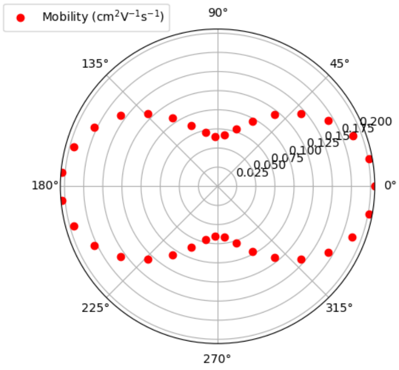




4-aza[6]helicene

ab plane





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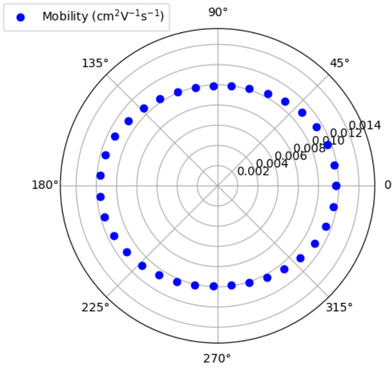

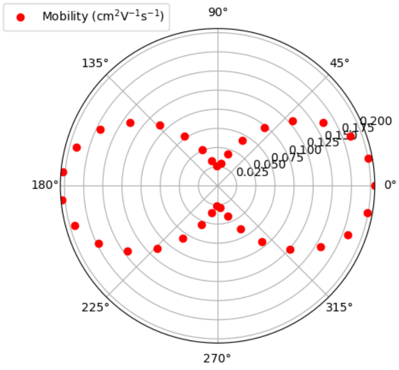

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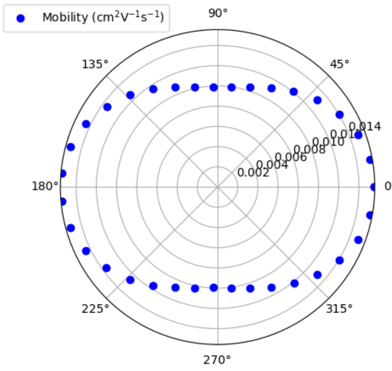
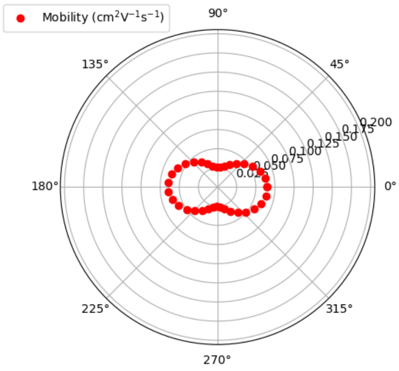
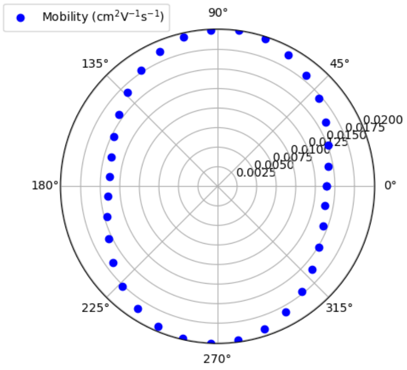
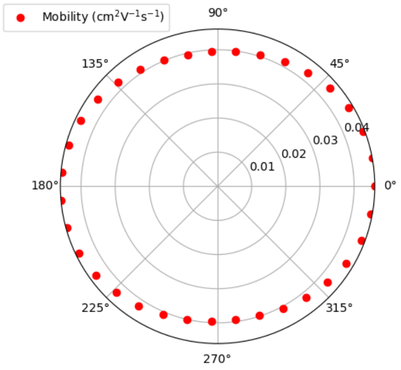




5-aza[6]helicene

ab plane





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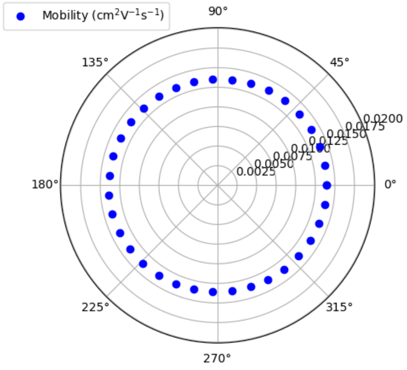
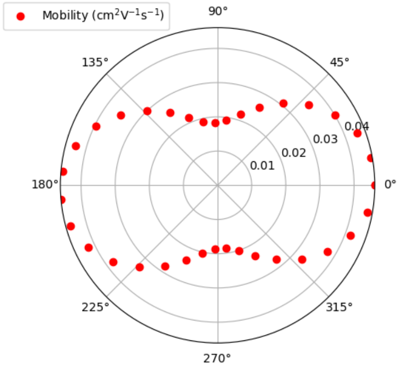
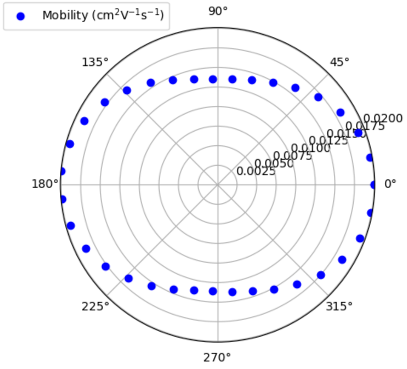
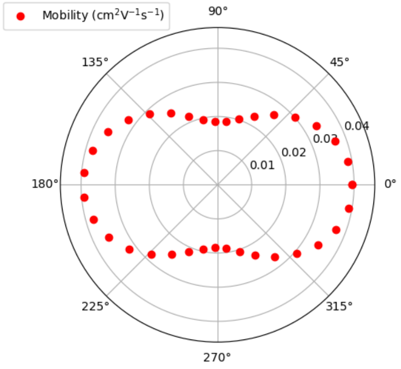




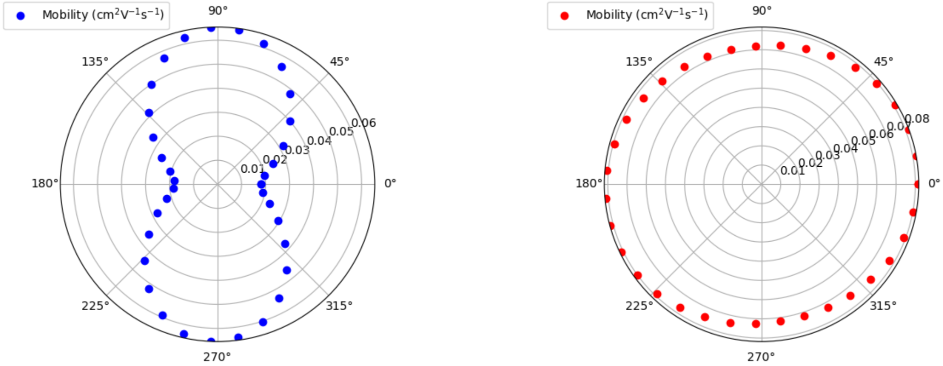
bc plane



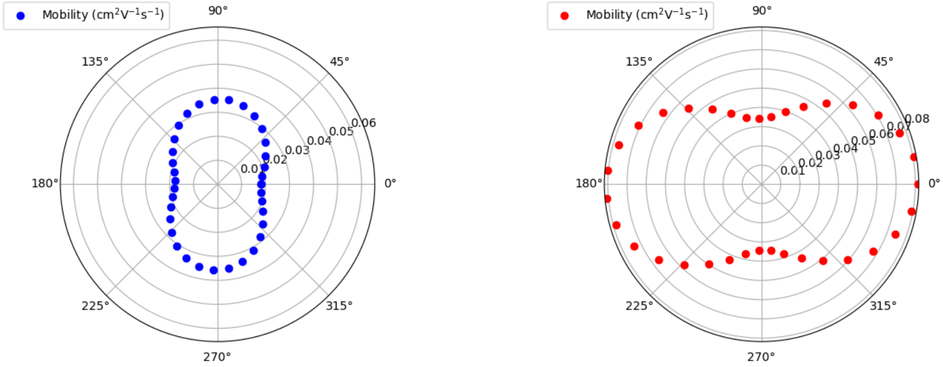


6-aza[6]helicene

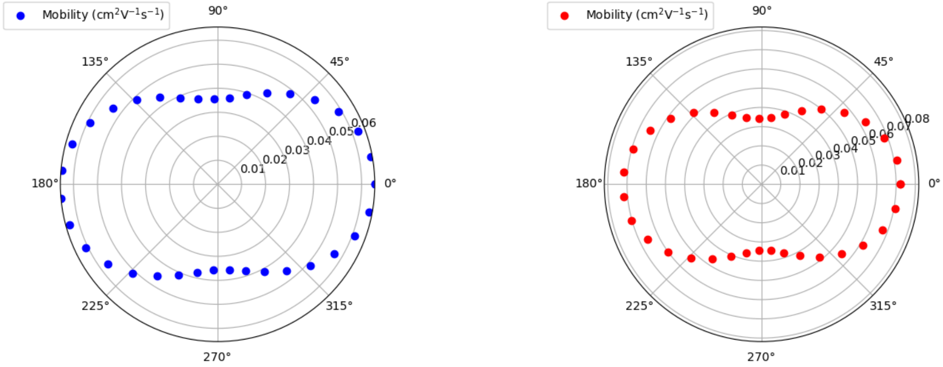
ab plane



ac plane

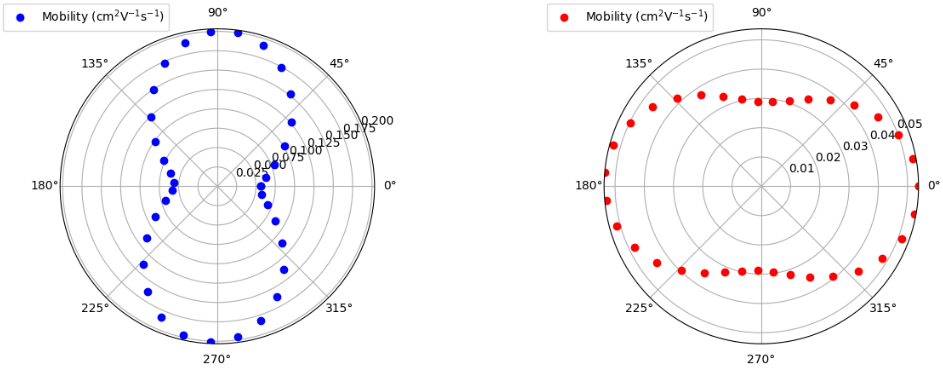


bc plane

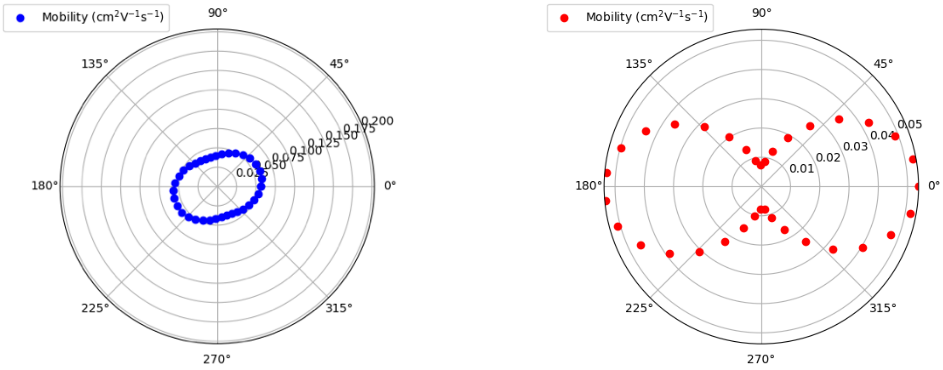


7-aza[6]helicene

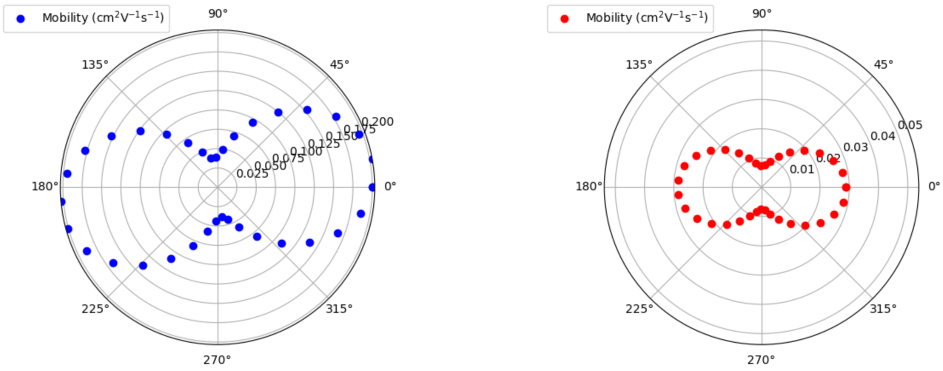
ab plane



ac plane

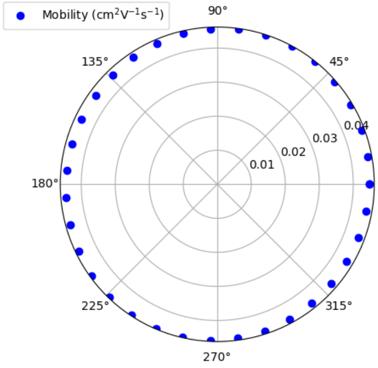


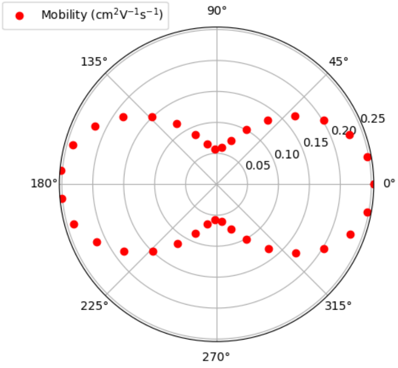
bc plane



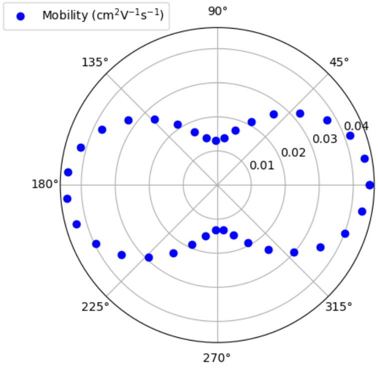
8-aza[6]helicene

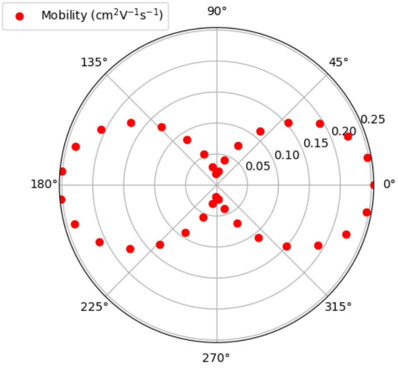
ab plane



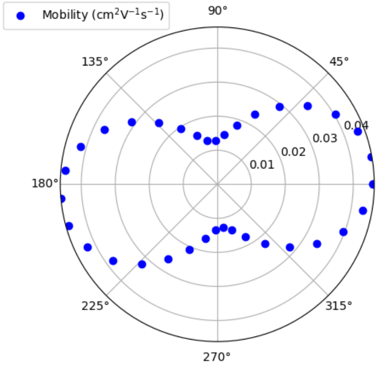


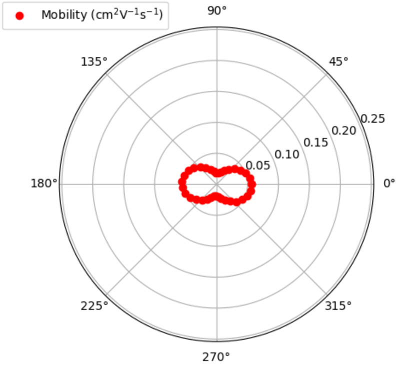
ac plane





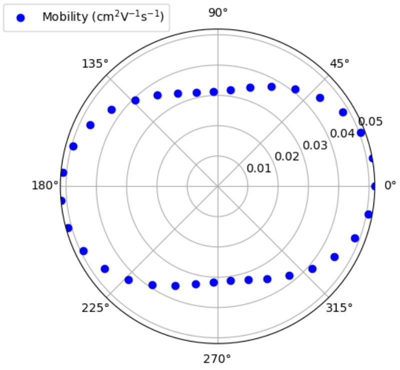
bc plane

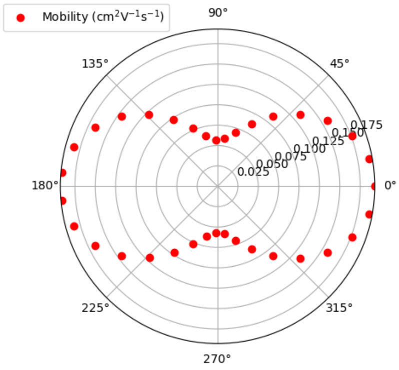




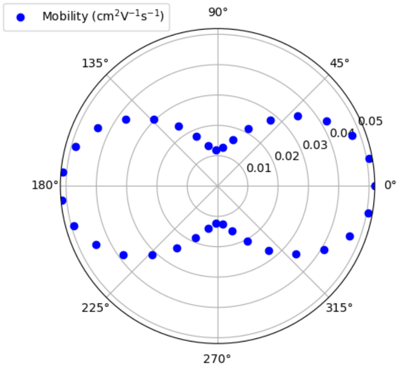
9-aza[6]helicene

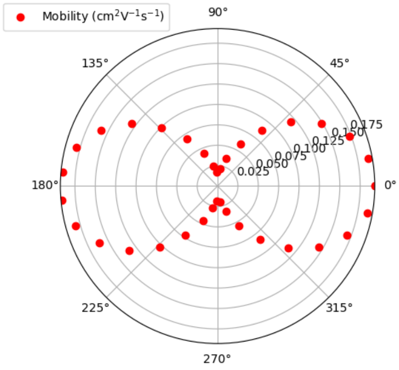
ab plane



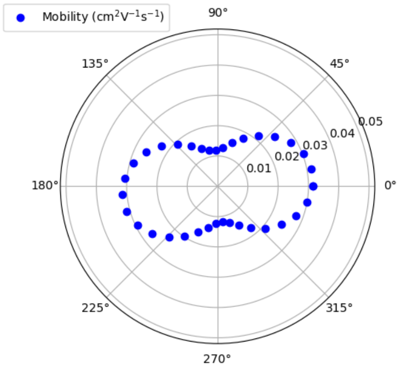


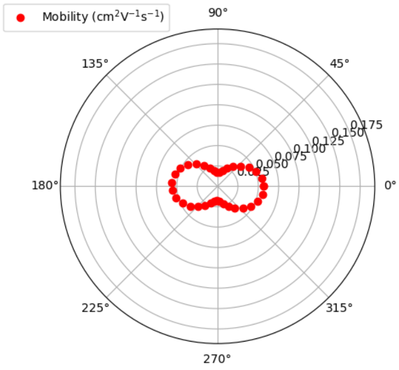
ac plane





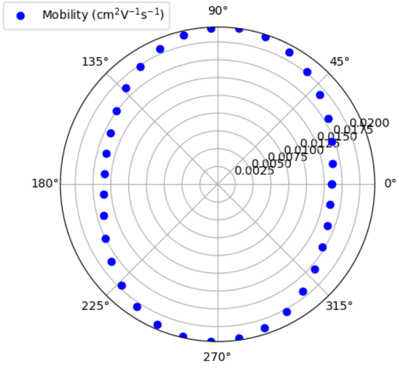
bc plane

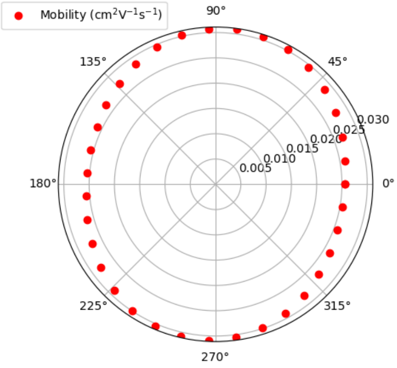




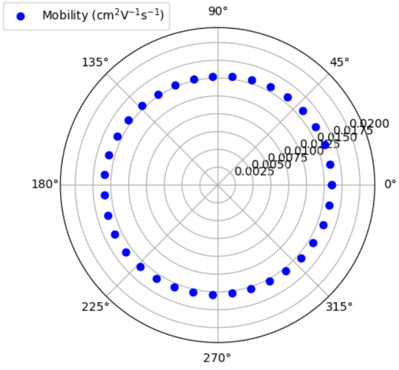
10-aza[6]helicene

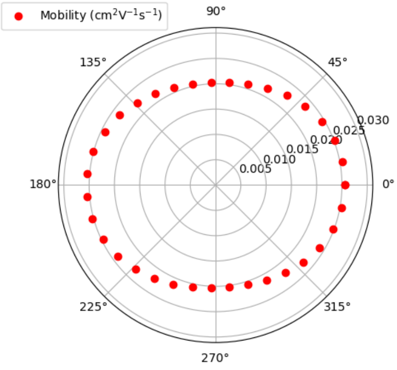
ab plane



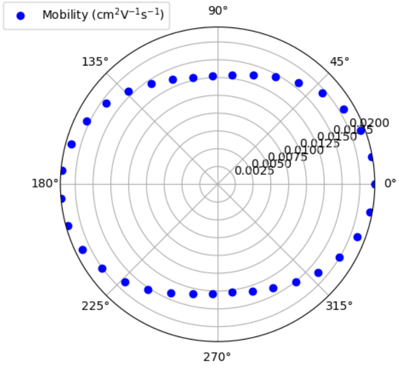


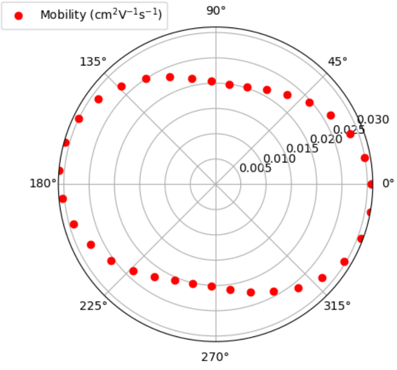
ac plane





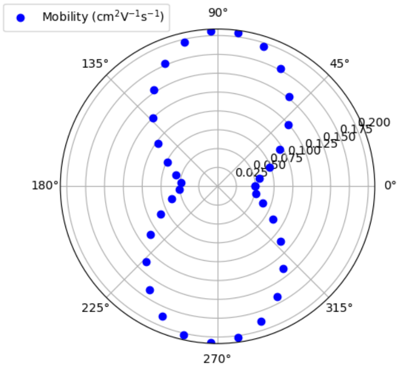
bc plane

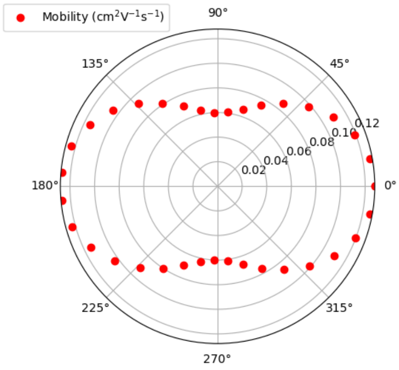




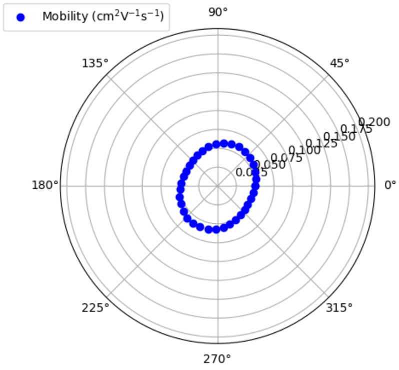
11-aza[6]helicene

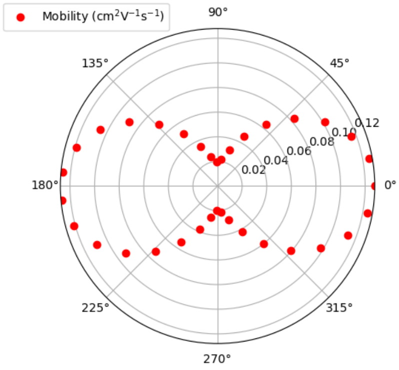
ab plane



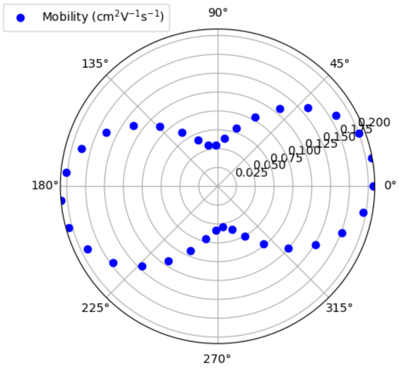


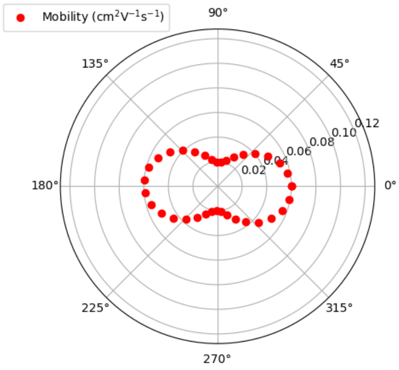
ac plane





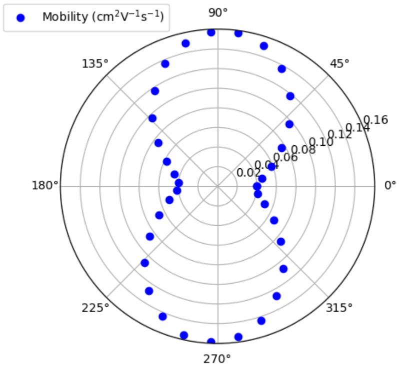
bc plane

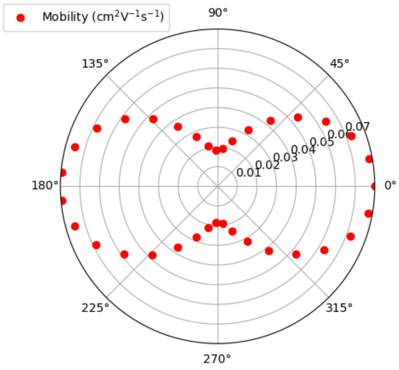




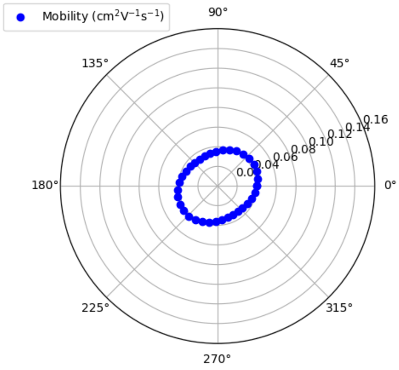
12-aza[6]helicene

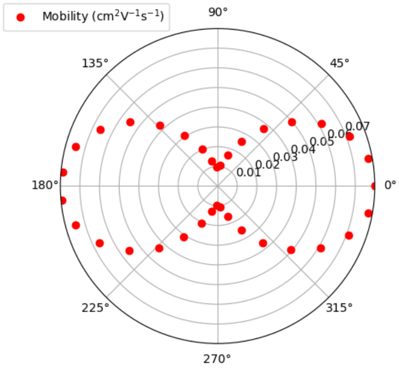
ab plane



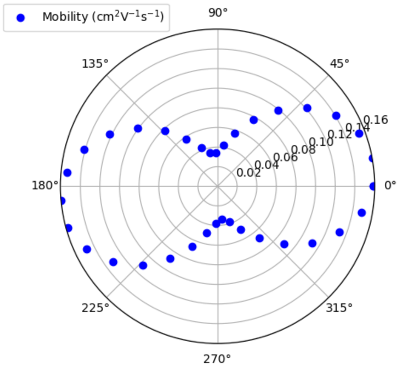


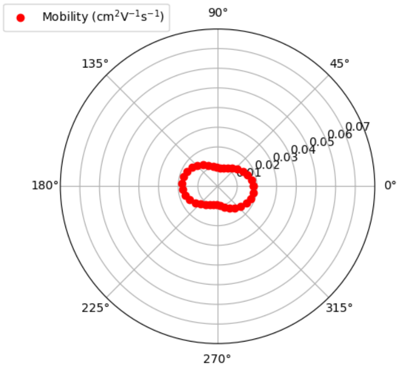
ac plane





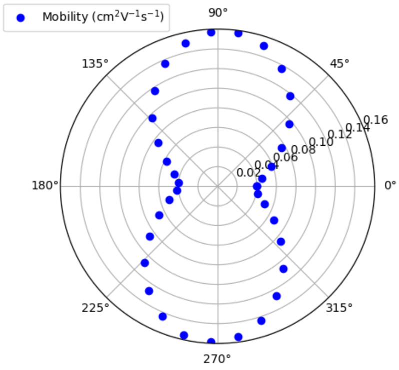
bc plane

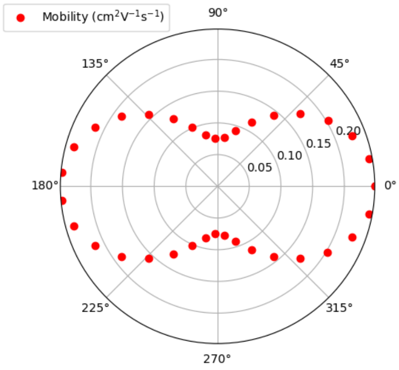




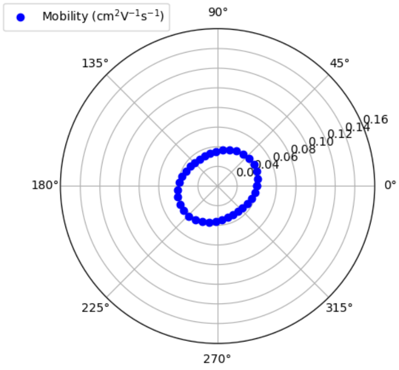
13-aza[6]helicene

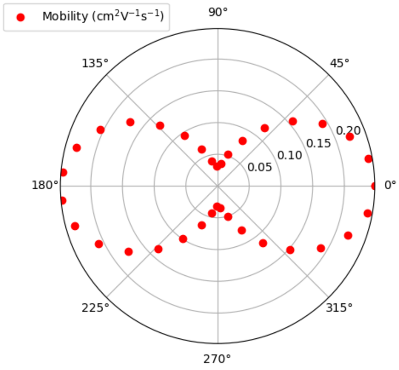
ab plane





ac plane





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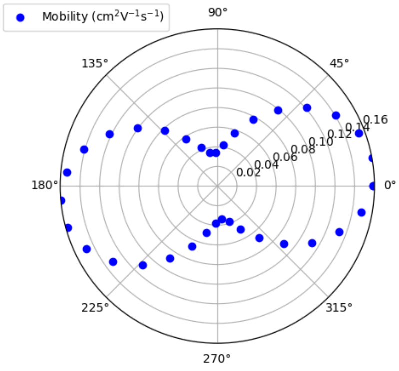
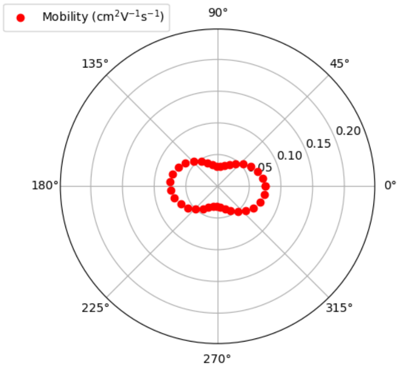
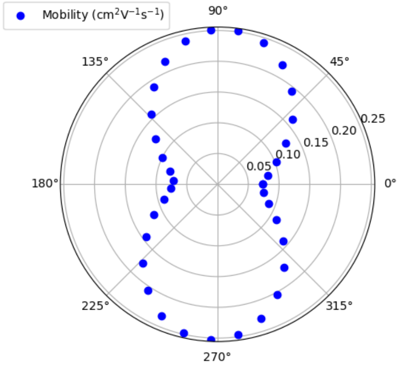
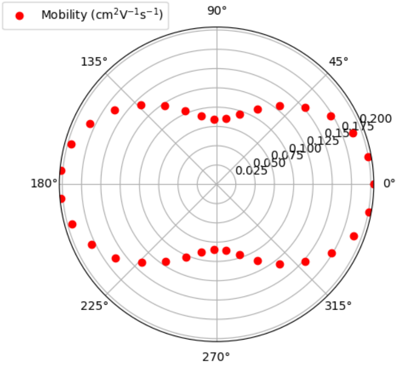




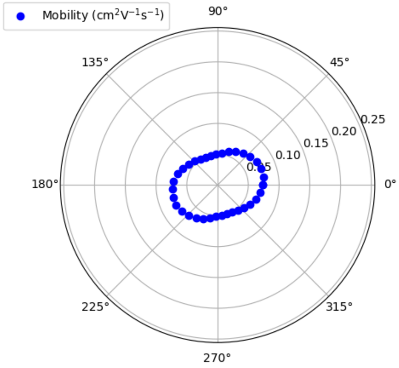
14-aza[6]helicene

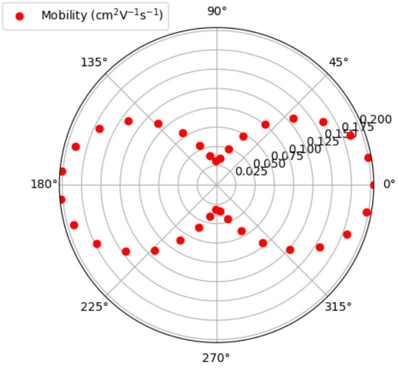
ab plane





ac plane





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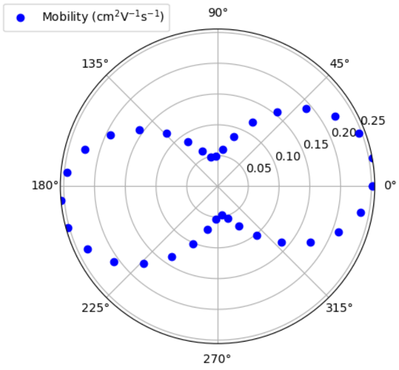
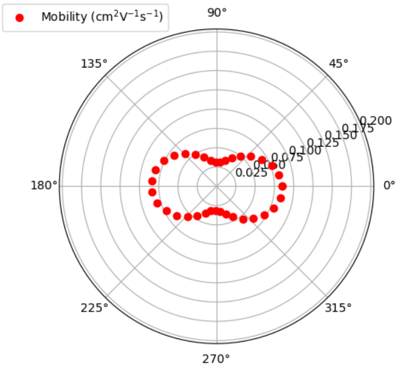
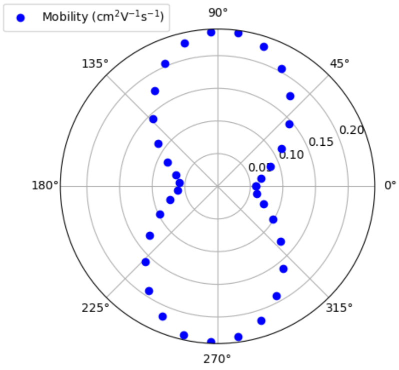
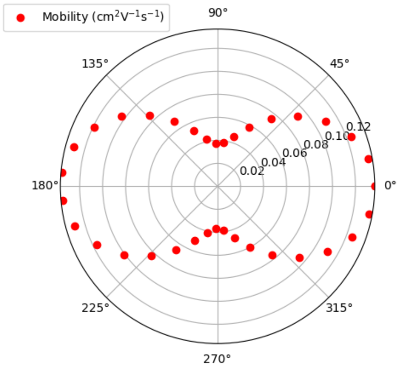




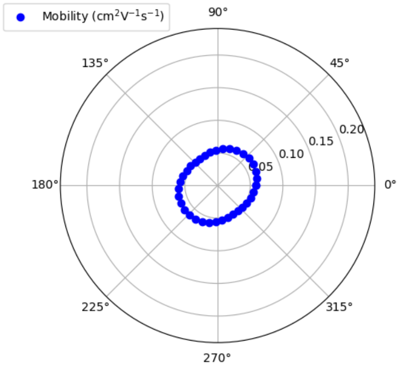
15-aza[6]helicene

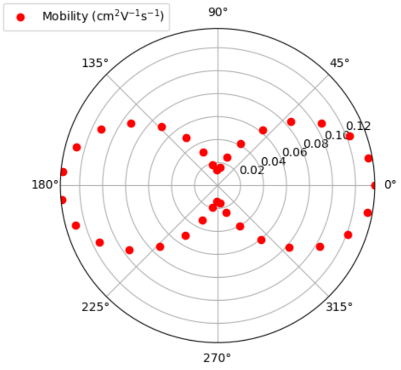
ab plane



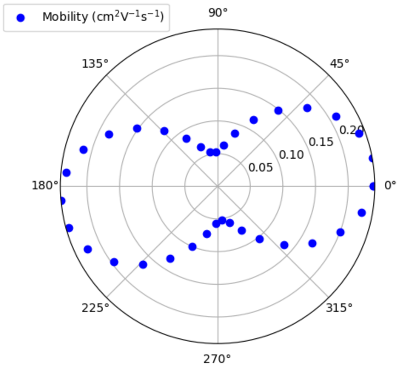


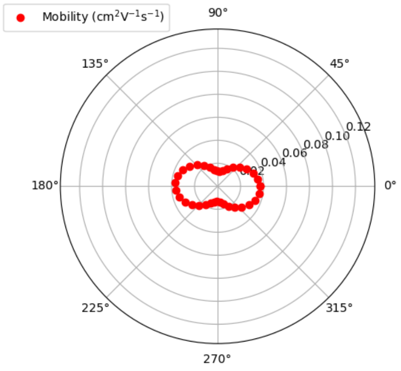
ac plane





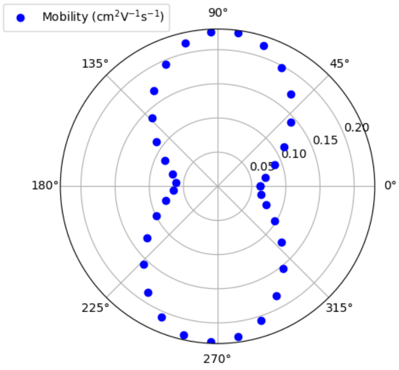
bc plane

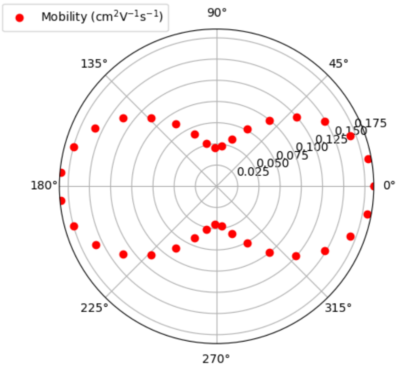




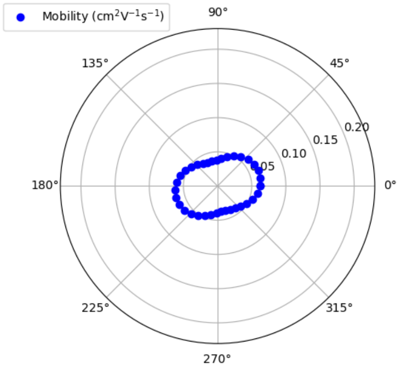
16-aza[6]helicene

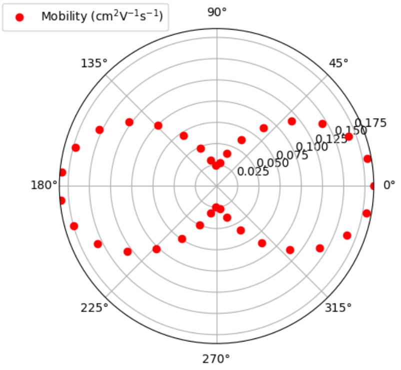
ab plane



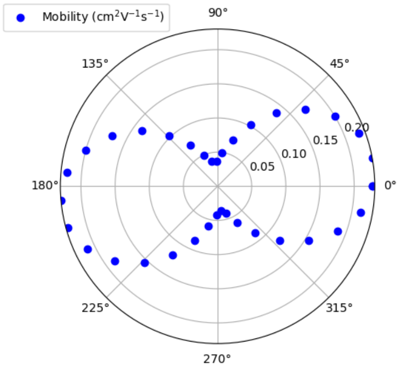


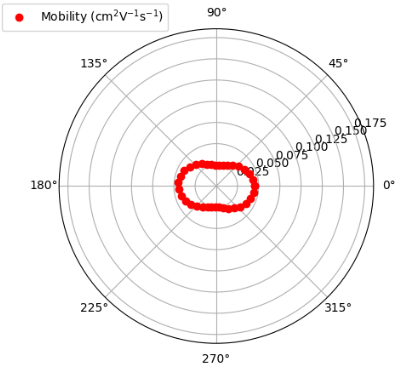
ac plane





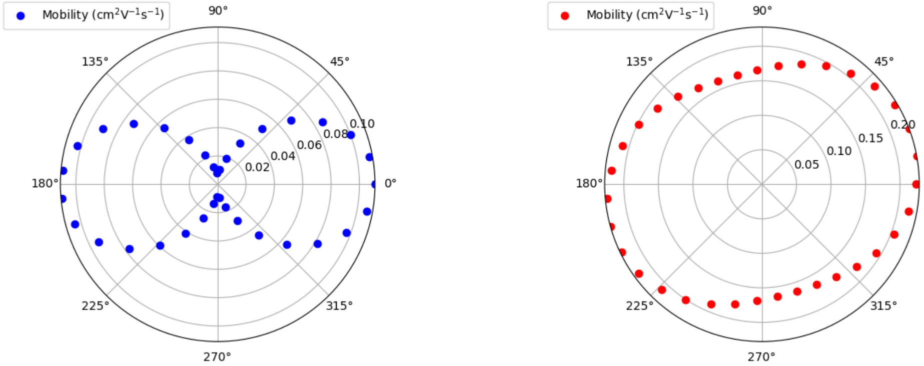
bc plane



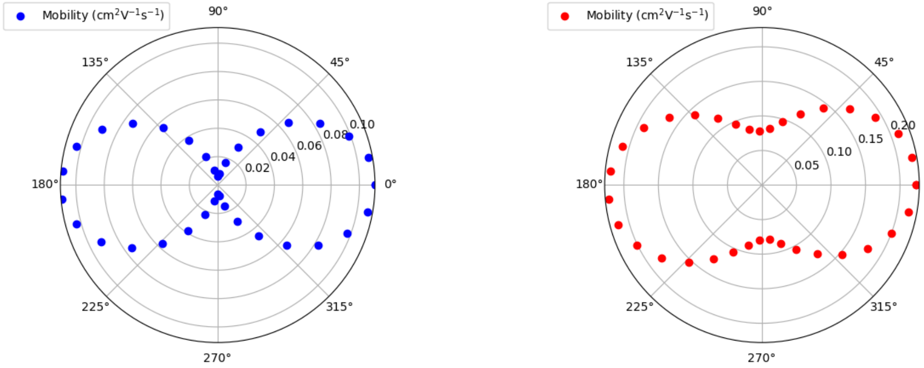


1,16-diaza[6]helicene

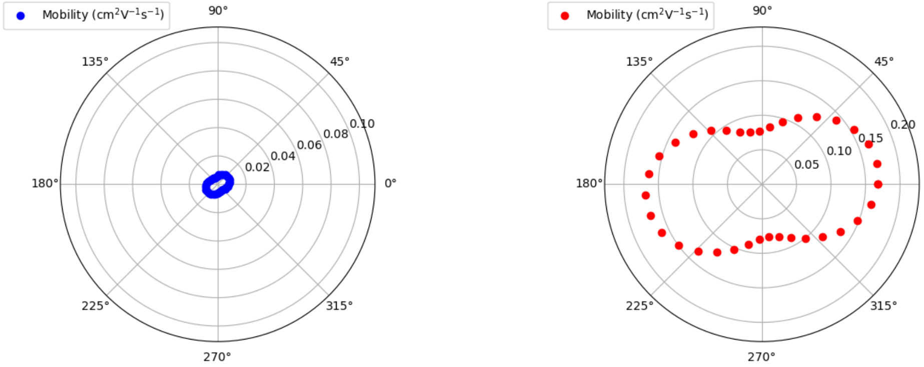
ab plane



ac plane



bc plane



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2 K. Sakanoue, M. Motoda, M. Sugimoto and S. Sakaki, *J. Phys. Chem. A*, 1999, **103**, 5551–5556.
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