

MorphCT Results - PAHs

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1 Latest Jobs, 12/17

The latest flurry of jobs involve a complete rerunning of the 7 PAH jobs we particularly care about. In the past, we ran into issues comparing the results because some of the systems contained rigid molecules, which automatically have $\Delta E_{ij} = 0$. Since the Marcus hopping rate equation:

$$k_{ij} = \frac{2\pi}{\hbar} T_{ij}^2 \sqrt{\frac{1}{4\lambda_{ij}\pi k_B T}} \exp -\frac{(\Delta E_{ij} + \lambda_{ij})^2}{4\lambda_{ij} k_B T}, \quad (1)$$

decays exponentially for $\Delta E_{ij} > -\lambda_{ij}$, this suppresses the hopping rate, resulting in lower mobilities (not larger as I said). Either way, we were comparing apples to oranges and at the very least we needed to make everything flexible to make it as realistic as possible.

As an ‘extension task’, we added charges in too, to improve model accuracy. The PE charges were taken from Mitch’s previous work, and the PT charges were calculated from quantum-chemical methods using NWChem.

How confident are we in the PE charges?

2 Mobility Results

ID	Simulation Name	Density (g cm ⁻³)	Anisotropy (Arb. U.)	Stacks (Arb. U.)	Mobility (cm ² V ⁻¹ s ⁻¹)
1	PE_MultiStack_Eclipsed	1.06	0.0594	1	8.81×10^0
2	PE_SingleStack_Eclipsed	1.06	0.0893	3	8.84×10^0
3	PE_SingleStack_Ordered	1.06	0.0471	195	8.95×10^0
4	PT_MultiStack_Eclipsed	1.01	0.1704	20	1.92×10^0
5	PT_MultiStack_Ordered	1.01	0.0906	63	1.27×10^0
6	PT_SingleStack_Eclipsed	1.01	0.0979	4	5.19×10^0
7	PT_SingleStack_Ordered	1.01	0.0267	63	1.55×10^0

Table 1: The results from MorphCT for the various PAH morphologies. See the below section for a discussion of the stacks.

TODO: Check the Stack definitions, some of the numbers seem off, especially for the ordered morphologies

2.1 Conclusions

- Exploring the ΔE_{ij} has shown that some of the systems (namely PE_MultiStack_Eclipsed, PT_SingleStack_Eclipsed, and PE_SingleStack_Ordered) contain rigid bodies (delta function for the DoS), whereas others don't. Having a $\Delta E_{ij} = 0$ will strongly affect (increase) the eventual hopping rate and so we are comparing apples to oranges.
- Additionally, while the PT_SingleStack systems are truly one single stack, the PE_SingleStack systems are not. They certainly have fewer stacks, but they are not on massive periodic structure like in the PT_SingleStack case, and so a direct comparison can not really be drawn there either.
- The carrier termination (anisotropy) graphs in panel 5) show that carriers have not moved very far out of the simulation volume in the PT_MultiStack, and PE_SingleStack_Eclipsed cases. All of the MSD fits are excellent, however, so this might not be an issue.
- All of the flexible PT_MultiStack and PE_SingleStack systems shown Gaussian DoSes with the maximum breadth permitted by the Gaussian map that we perform in MorphCT (which will shrink a distribution with $\sigma > 100\text{meV}$ down to $\sigma = 100\text{meV}$, but leave distributions with $\sigma \leq 100\text{meV}$ alone). The breadth of the Ordered system is significantly greater than the Eclipsed system, in both cases. This makes sense - in the Eclipsed case, the molecules are azimuthally in-register and so are squeezed into planarity by the molecules closely packed around it. This makes each molecule structurally indistinct, which manifests as an energetic indistinction and the $\Delta E_{ij} \rightarrow 0$.

I think there are too many variables here that we are unable to resolve with just these 7 simulations. This makes it impossible to draw any conclusions about the presence and orientation of the stacks other than “[it matters and can affect the mobilities by an order of magnitude](#)”. Given the strict mathematical constraints on how the stacks can form and still produce a coherent structure without morphological defects, I am not convinced that this is something we can adjust our mobilities for either. Instead, I think it's something that we just have to be aware of when submitting our simulations to KMC, consider when drawing conclusions, and disclose fully when we present results.

dyFix_imageFix_relaxed_PE_MultiStack_Eclipsed_UA

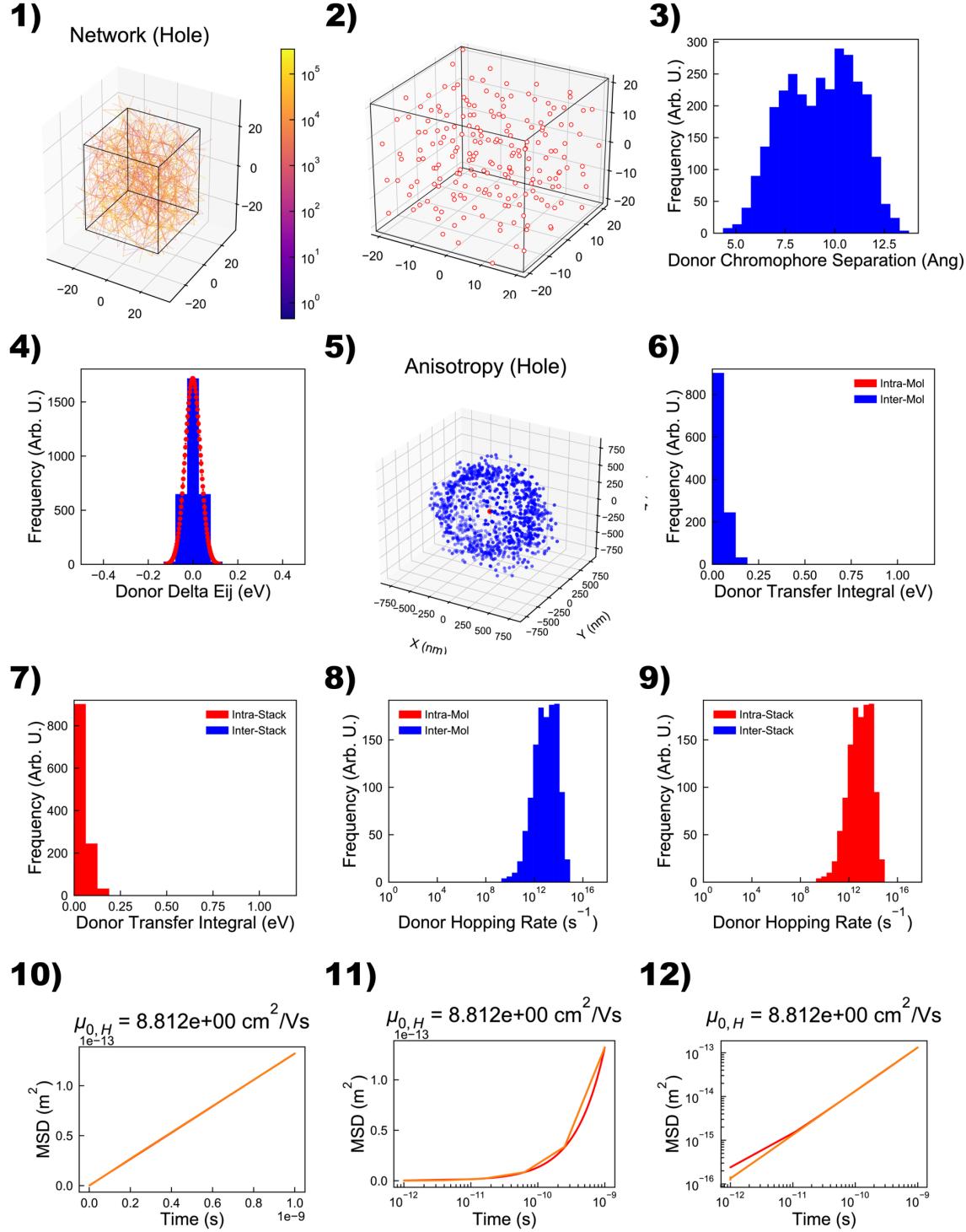


Figure 1: 1) Chromophore connectivity network, 2) Location of 'stacks', 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (delta Eij), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

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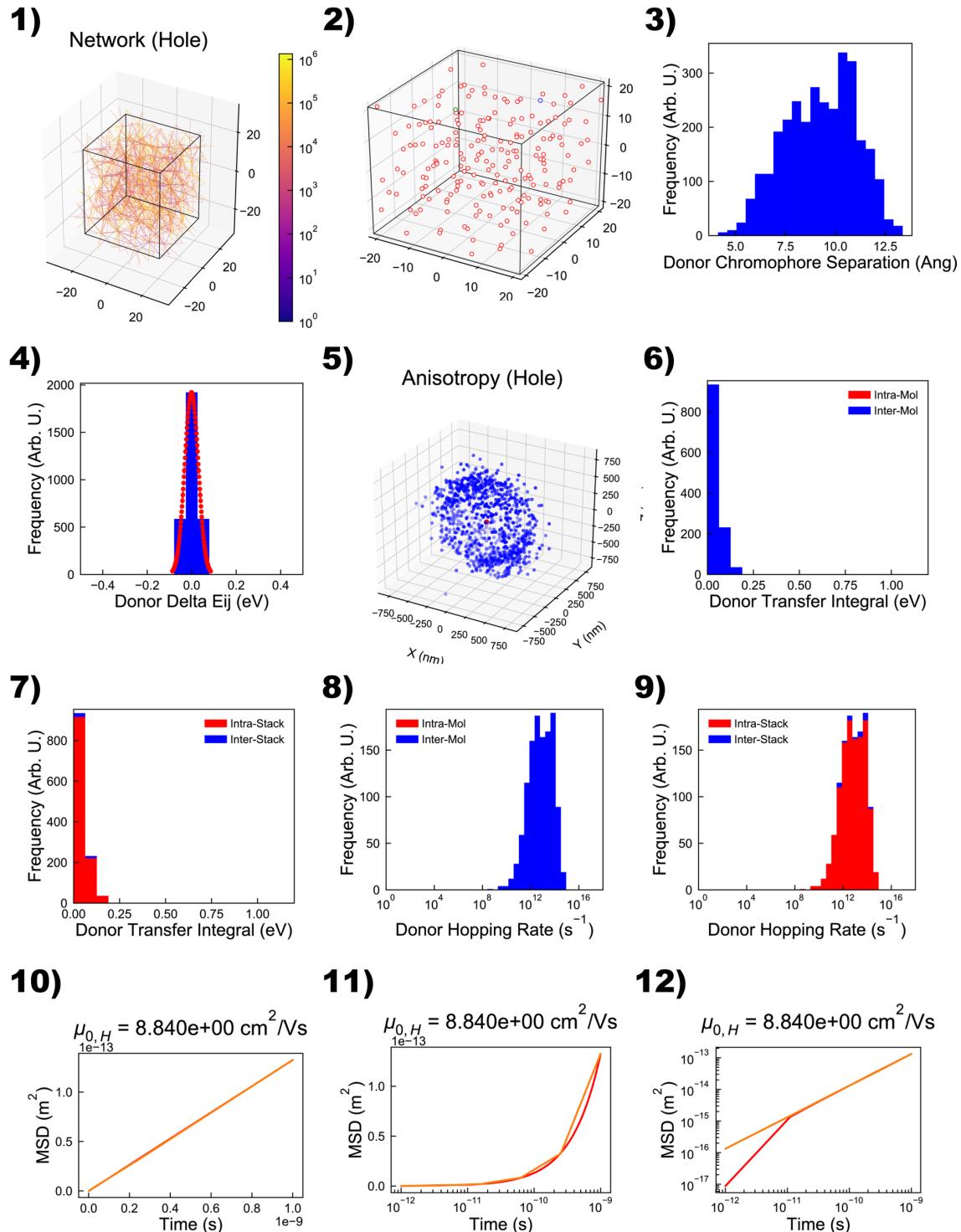


Figure 2: 1) Chromophore connectivity network, 2) Location of 'stacks', 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (ΔE_{ij}), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

lyFix_imageFix_relaxed_PE_SingleStack_Ordered_UA

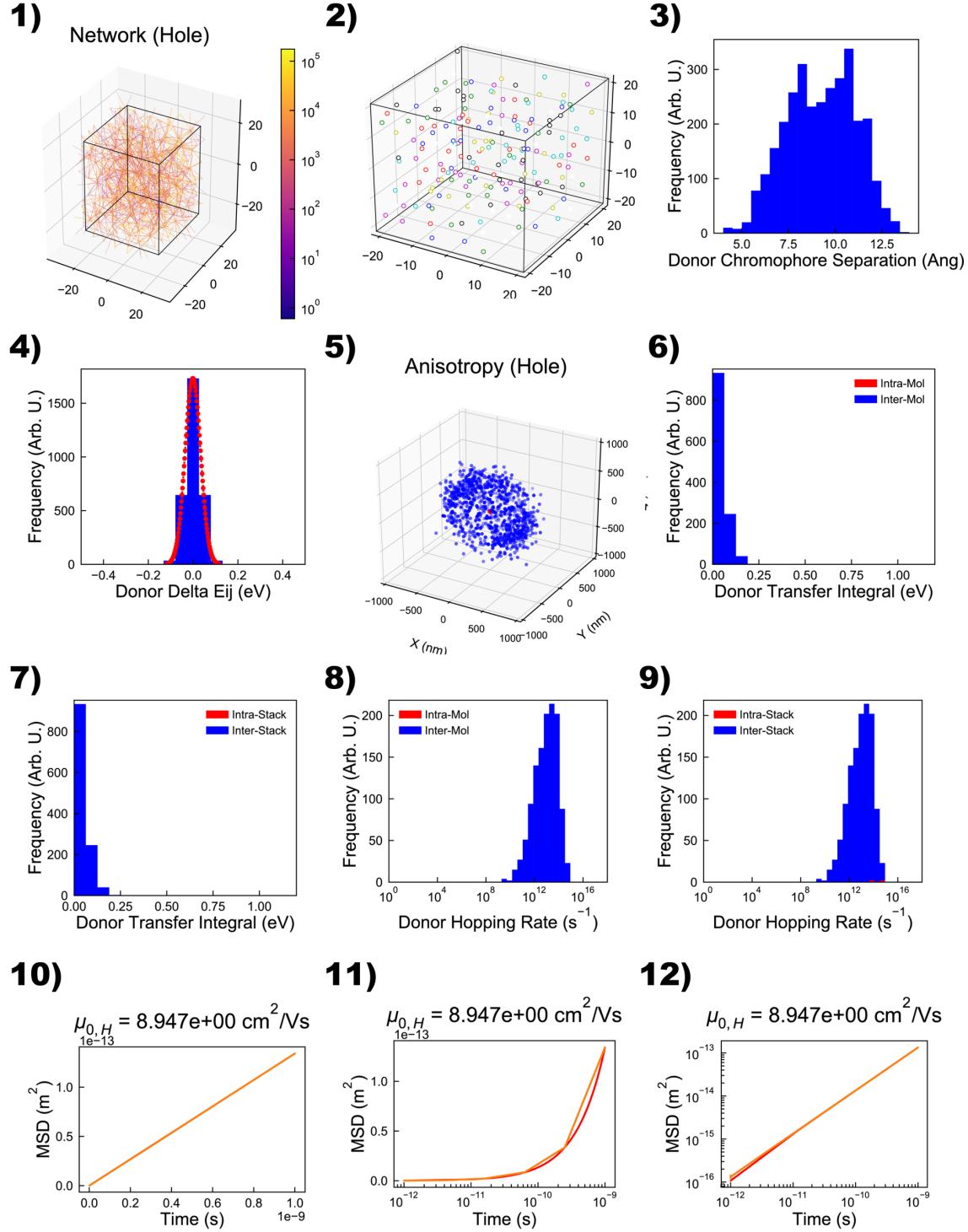


Figure 3: 1) Chromophore connectivity network, 2) Location of ‘stacks’, 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (ΔE_{ij}), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

dyFix_imageFix_relaxed_PT_MultiStack_Eclipsed_UA

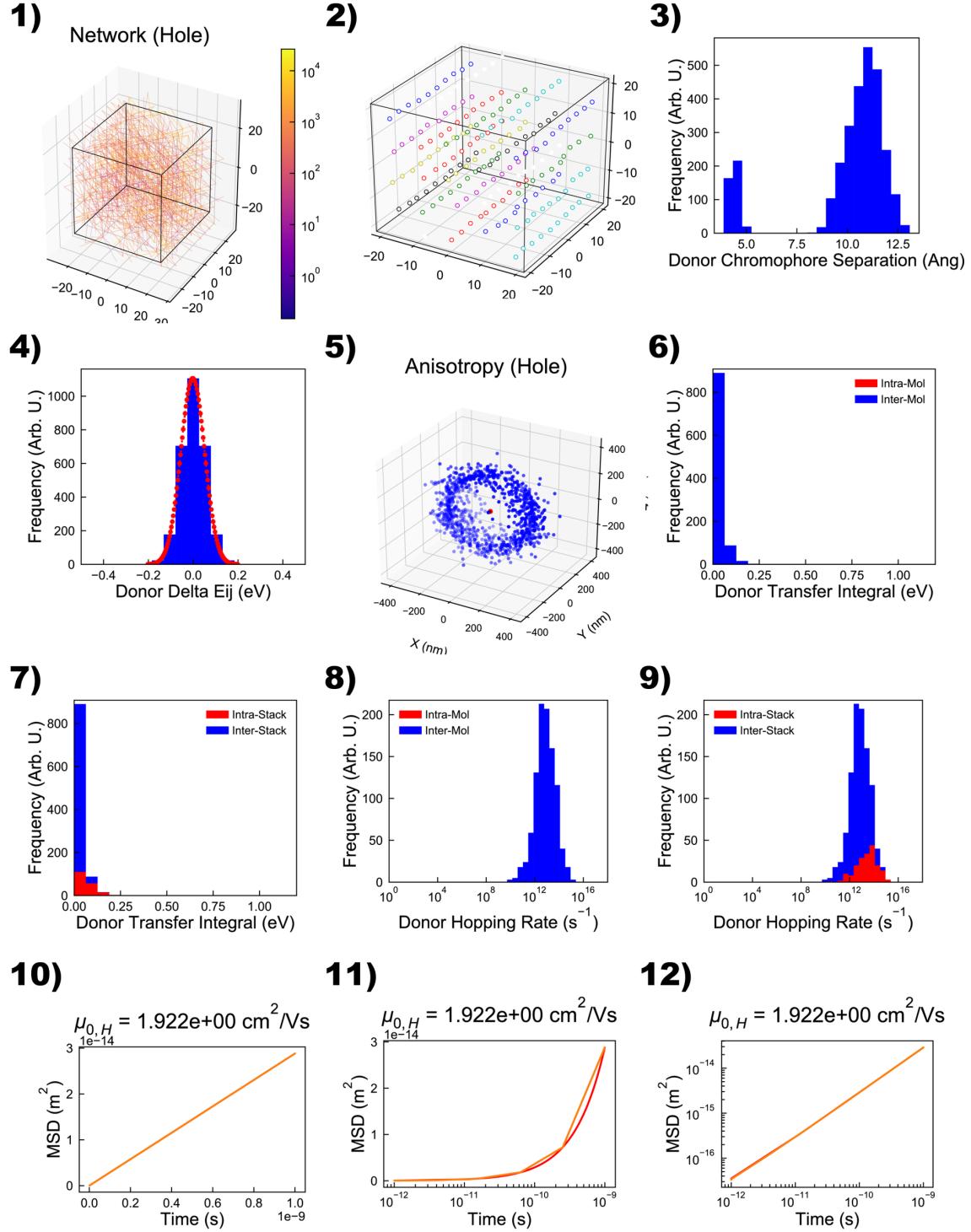


Figure 4: 1) Chromophore connectivity network, 2) Location of 'stacks', 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (delta Eij), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

dyFix_imageFix_relaxed_PT_MultiStack_Ordered_UA

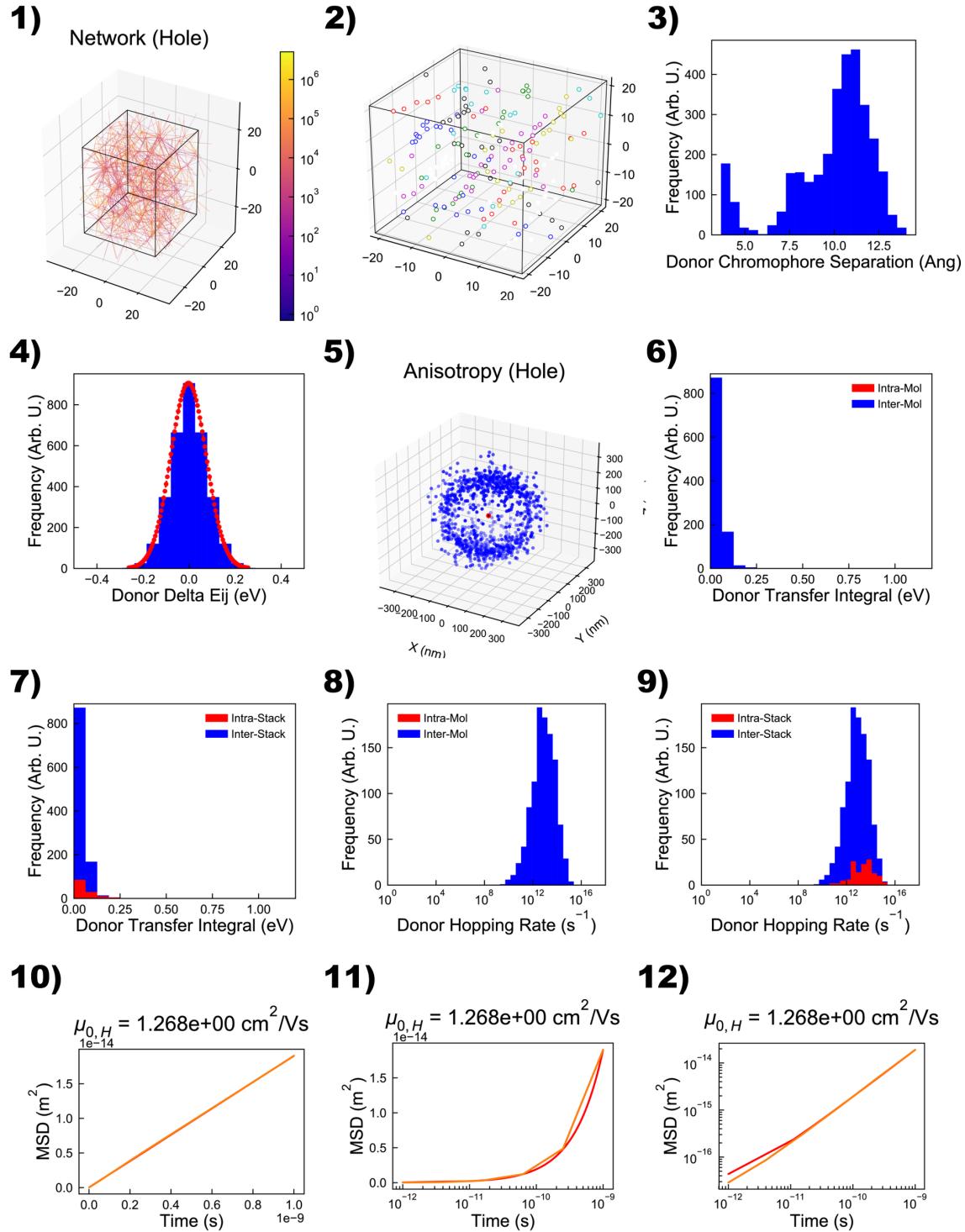


Figure 5: 1) Chromophore connectivity network, 2) Location of ‘stacks’, 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (ΔE_{ij}), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

lyFix_imageFix_relaxed_PT_SingleStack_Eclipsed_UA

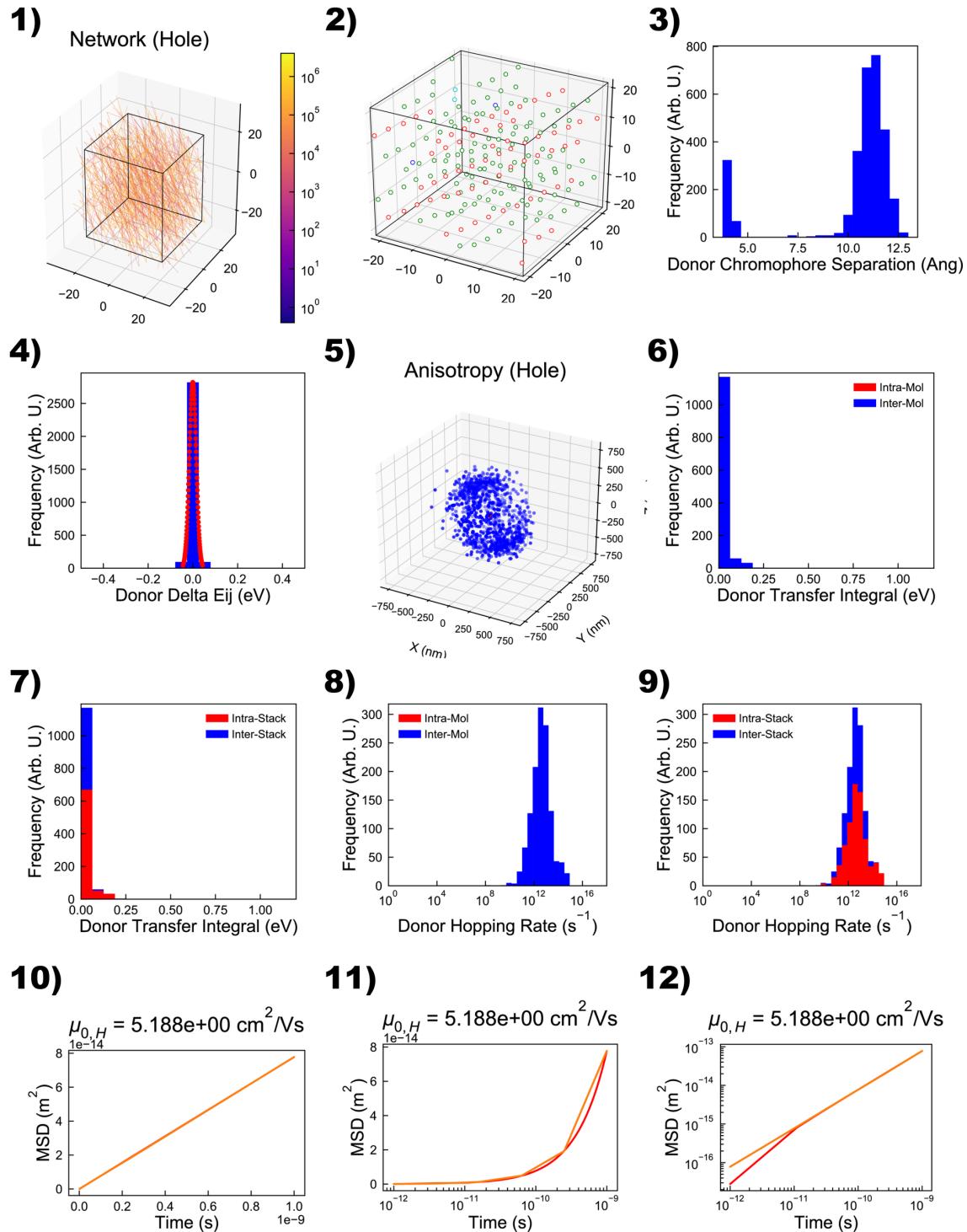


Figure 6: 1) Chromophore connectivity network, 2) Location of ‘stacks’, 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (ΔE_{ij}), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.

lyFix_imageFix_relaxed_PT_SingleStack_Ordered_UA

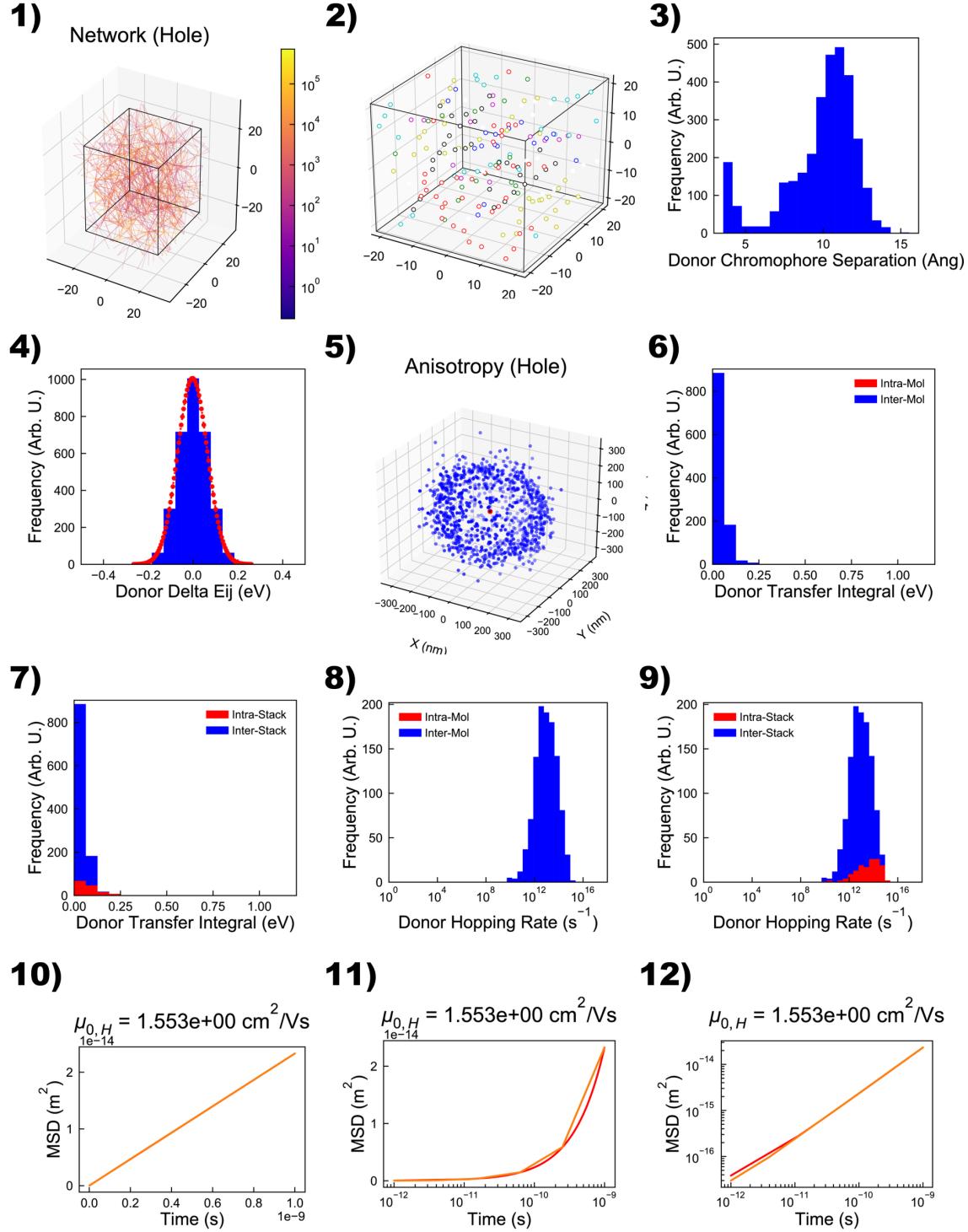


Figure 7: 1) Chromophore connectivity network, 2) Location of 'stacks', 3) Distribution of connected chromophore separations (defines stacks), 4) Density of states of Frontier molecular orbital (delta Eij), 5) KMC Carrier termination locations (defines anisotropy), 6) Histogram of molecular transfer integrals, 7) Histogram of stack transfer integrals, 8) Histogram of molecular hopping rates, 9) Histogram of stack hopping rates, 10) Linear MSD plot, 11) Semi-log-x MSD plot, 12) Logarithmic MSD plot.