

Supporting Information

Impact of Morphology, Side-Chains, and Crystallinity on Charge-Transport Properties of π -Extended Double Helicenes

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1. Calculation of hole mobilities by transient localization model

To validate our approach, we also calculated mobilities using the transient localization model, as defined by:

$$\mu = \frac{q}{k_B T} \frac{L^2}{2\tau} \text{ (Equation S1)}$$

where L is the localization length (in units of lattice spacing) and τ is the intermolecular fluctuation time.

As mentioned in the main text, $2\pi\tau$ is taken to be 1 ps in all cases.[S1] Using the J values given in Table 1 and from the map of the transient localization lengths in disordered systems as described in ref. S1, we calculated hole mobilities of **DH1**, **DH2**, and **DH3**. We note that this model is in fact unsuitable for **DH3** due to the three-dimensional transport network, but for completeness we predict the transport along the (010) plane (Figure 1).[S1] Localization is mapped on J -space and linked to angle defined as:

$$\theta = \arccos\left(\frac{J_a}{\sqrt{J_a^2 + J_b^2 + J_c^2}}\right) \text{ (Equation S2)}$$

where J_a , J_b , and J_c values represent the average electronic coupling along different transport directions. θ values of **DH1**, **DH2** and **DH3** are found to be 0.28, 0.84 and 0.0, respectively. From those values, localization lengths (L^2) were calculated to be 7.2, 21.0 and 2.4 for **DH1**, **DH2** and **DH3**, respectively.

2. DFT-optimized geometries of DH1, DH2, and DH3

All geometries were fully optimized at the B3LYP/6-311G(d,p) level of theory in the gas phase.[S2,S3,S4,S5] All optimized geometries were verified by frequency computations as minima (no imaginary frequencies). All quantum chemical computations were performed using Gaussian 09.[S6]

DH1

C	4.92320	-0.71111	0.17593
C	6.10828	-1.45165	0.21886
H	7.04782	-0.98742	-0.04789
C	6.10093	-2.79854	0.55925
H	7.02866	-3.35942	0.56120
C	4.91322	-3.42507	0.89638
H	4.93076	-4.47326	1.16167
C	3.69766	-2.72566	0.87276
C	3.69208	-1.36526	0.45659
C	2.44705	-3.33255	1.31192
C	2.43070	-4.55548	2.01573
H	3.35846	-5.08109	2.19740
C	1.26257	-5.07983	2.52905
H	1.28191	-6.01646	3.07459
C	0.06459	-4.37051	2.38116
H	-0.85157	-4.74428	2.82367
C	0.05308	-3.17808	1.68855
H	-0.87355	-2.62897	1.61582
C	1.22401	-2.64576	1.10216
C	2.44018	-0.67722	0.24320
C	1.22437	-1.36514	0.39425
C	-0.00001	-0.70850	0.00002
C	-1.22439	-1.36516	-0.39419
C	-1.22400	-2.64581	-1.10204
C	-0.05304	-3.17818	-1.68834
H	0.87359	-2.62906	-1.61559
C	-0.06451	-4.37064	-2.38087
H	0.85168	-4.74445	-2.82330
C	-1.26248	-5.07998	-2.52877
H	-1.28179	-6.01666	-3.07422
C	-2.43064	-4.55558	-2.01556
H	-3.35840	-5.08123	-2.19724
C	-2.44704	-3.33259	-1.31185
C	-3.69767	-2.72564	-0.87286
C	-4.91327	-3.42498	-0.89672
H	-4.93083	-4.47318	-1.16208
C	-6.10101	-2.79841	-0.55979
H	-7.02878	-3.35923	-0.56198
C	-6.10834	-1.45155	-0.21929
H	-7.04796	-0.98725	0.04728
C	-4.92322	-0.71108	-0.17605
C	-3.69209	-1.36525	-0.45663
C	-2.44020	-0.67723	-0.24318
C	4.92320	0.71111	-0.17593
C	6.10828	1.45165	-0.21886

H	7.04782	0.98742	0.04789
C	6.10093	2.79854	-0.55925
H	7.02866	3.35942	-0.56120
C	4.91322	3.42507	-0.89638
H	4.93076	4.47326	-1.16167
C	3.69766	2.72566	-0.87276
C	3.69208	1.36526	-0.45659
C	2.44705	3.33255	-1.31192
C	2.43070	4.55548	-2.01573
H	3.35846	5.08109	-2.19740
C	1.26257	5.07983	-2.52905
H	1.28191	6.01646	-3.07459
C	0.06459	4.37051	-2.38116
H	-0.85157	4.74428	-2.82367
C	0.05308	3.17808	-1.68855
H	-0.87355	2.62897	-1.61582
C	1.22401	2.64576	-1.10216
C	2.44018	0.67722	-0.24320
C	1.22437	1.36514	-0.39425
C	-0.00001	0.70850	-0.00002
C	-1.22439	1.36516	0.39419
C	-1.22400	2.64581	1.10204
C	-0.05304	3.17818	1.68834
H	0.87359	2.62906	1.61559
C	-0.06451	4.37064	2.38087
H	0.85168	4.74445	2.82330
C	-1.26248	5.07998	2.52877
H	-1.28179	6.01666	3.07422
C	-2.43064	4.55558	2.01556
H	-3.35840	5.08123	2.19724
C	-2.44704	3.33259	1.31185
C	-3.69767	2.72564	0.87286
C	-4.91327	3.42498	0.89672
H	-4.93083	4.47318	1.16208
C	-6.10101	2.79841	0.55979
H	-7.02878	3.35923	0.56198
C	-6.10834	1.45154	0.21929
H	-7.04796	0.98725	-0.04728
C	-4.92322	0.71108	0.17605
C	-3.69209	1.36525	0.45663
C	-2.44020	0.67723	0.24318

DH2

C	2.66698200	0.79277600	1.07586400
C	3.03091200	-0.42277200	1.69613600
H	2.36507000	-1.27066400	1.61875400
C	4.18796600	-0.56976900	2.44413800
C	5.02295400	0.55129100	2.59316100
H	5.92603600	0.47436100	3.18929500
C	4.67626400	1.76466400	2.03697800
H	5.30840400	2.62091100	2.23093400
C	3.49624400	1.92375300	1.28262600

C	3.07430400	3.22927400	0.79402900
C	3.93238200	4.33879200	0.80343600
H	4.96478500	4.22345800	1.10434100
C	3.48354600	5.58788300	0.40902000
H	4.16502400	6.43094500	0.40189000
C	2.16102800	5.76508900	0.02284300
H	1.83896900	6.74931700	-0.28772400
C	1.26634200	4.69078300	-0.00652500
C	1.73698200	3.39381700	0.33765600
C	-0.95040600	3.72987300	-0.63593100
C	-0.13177900	4.87060300	-0.40599400
C	-0.69191400	6.14421800	-0.54332800
H	-0.10359400	7.02386200	-0.32168000
C	-2.01806900	6.30836100	-0.92374100
H	-2.43784400	7.30493800	-0.99990400
C	-2.80411500	5.20379200	-1.20298200
H	-3.83403900	5.35496300	-1.49548900
C	-2.28893400	3.90414100	-1.08533300
C	-3.06783300	2.73013900	-1.45319000
C	-4.27483100	2.84441700	-2.17475100
H	-4.65337500	3.82408300	-2.43356200
C	-4.96616500	1.73621200	-2.61145600
H	-5.88335800	1.86392600	-3.17752400
C	-4.46462100	0.44314500	-2.37718500
C	-3.28308700	0.32155800	-1.66776800
H	-2.87606600	-0.66951700	-1.52906600
C	-2.57555200	1.43437100	-1.15679700
C	-1.30335100	1.29103700	-0.44580300
C	-0.45164400	2.40586400	-0.34684800
C	0.88873800	2.23941400	0.15293400
C	1.40641900	0.94757300	0.34758400
C	0.59163300	-0.18708100	-0.01770900
C	-0.81234400	0.00379800	-0.00923100
C	-1.61656400	-1.11062100	0.43112800
C	-1.10096100	-2.41086400	0.29710400
C	0.23185500	-2.60442200	-0.21013100
C	1.07623100	-1.49537100	-0.39024700
C	2.33652300	-1.67932800	-1.11248600
C	3.01691100	-0.60073000	-1.72239700
H	2.59865400	0.39299700	-1.64903100
C	4.18283900	-0.76412200	-2.44983900
C	4.69890200	-2.06509200	-2.58980500
H	5.60532300	-2.22525900	-3.16501200
C	4.03292300	-3.14505800	-2.05249000
H	4.41904800	-4.13749800	-2.24316700
C	2.83751900	-2.98885300	-1.31980300
C	2.07294700	-4.13892900	-0.85701200
C	2.59671200	-5.44009100	-0.88002000
H	3.62711200	-5.60486200	-1.16421900
C	1.81844000	-6.52688400	-0.51970700
H	2.24529300	-7.52337000	-0.52312700
C	0.49049600	-6.34520000	-0.15360800
H	-0.09305800	-7.21011100	0.13077400
C	-0.07686300	-5.06822800	-0.10819500

C	0.73511400	-3.94196000	-0.41561900
C	-1.94782600	-3.55320800	0.54587800
C	-1.47702700	-4.86647300	0.27267600
C	-2.37520100	-5.93572700	0.34897800
H	-2.05217200	-6.93400400	0.08753400
C	-3.70105800	-5.73845100	0.71589800
H	-4.38444500	-6.57945700	0.74163700
C	-4.14910400	-4.47227200	1.04955400
H	-5.18318500	-4.33978600	1.33643500
C	-3.28650500	-3.36603700	0.99299500
C	-3.70148200	-2.04380900	1.42907600
C	-4.87605200	-1.86303000	2.20093100
H	-5.50212100	-2.71593100	2.42558500
C	-5.18225600	-0.65532500	2.77107700
H	-6.03499200	-0.54668900	3.43016000
C	-4.36228900	0.48446700	2.54457600
C	-3.22981400	0.31789100	1.72998600
H	-2.56885800	1.16080100	1.59730700
C	-2.86725900	-0.92401200	1.17237300
C	4.52769600	-1.89601500	3.08924600
H	3.60156200	-2.37384400	3.42364600
H	5.12381100	-1.72029900	3.99022100
C	5.26595900	-2.88363200	2.15586300
H	4.65186100	-3.03726800	1.26312800
H	5.32378200	-3.85449000	2.66351200
C	6.67771200	-2.46099300	1.72306100
H	7.01846400	-3.15558300	0.94734400
H	6.63428700	-1.47677100	1.24465700
C	-5.20896900	-0.77333500	-2.87791100
H	-4.52626300	-1.62793500	-2.91937900
H	-5.55145900	-0.59641200	-3.90443400
C	-6.42240400	-1.13667300	-2.00051000
H	-6.08137100	-1.30124200	-0.97215800
H	-7.10744000	-0.28103600	-1.96070200
C	-7.18005200	-2.37349600	-2.49618800
H	-6.49516500	-3.22948600	-2.52224900
H	-7.50345800	-2.21055800	-3.53163100
C	-8.39537900	-2.71784100	-1.63046300
H	-8.91212900	-3.60678500	-2.00241300
H	-9.11686400	-1.89506100	-1.61694600
H	-8.09959700	-2.91286000	-0.59501200
C	4.88979000	0.41553900	-3.07729300
H	4.16717600	1.21800900	-3.24847900
H	5.27576500	0.12522800	-4.06193100
C	6.05920100	0.94023300	-2.21933200
H	5.66591000	1.28601200	-1.25656200
H	6.72905900	0.10341500	-1.99168500
C	6.87224500	2.06315200	-2.88150800
H	7.74132100	2.27727900	-2.24918900
H	7.27528700	1.70150400	-3.83589200
C	6.09502100	3.36348000	-3.11521800
H	5.27048000	3.22700200	-3.81994200
H	6.74670900	4.14039800	-3.52463100
H	5.67034000	3.74277500	-2.18062000

C	-4.36336900	2.97066400	2.63924000
H	-3.65137800	2.95455800	1.79326200
H	-5.34984700	3.13517500	2.15283300
C	-4.08796800	4.15019500	3.58487800
H	-3.11143900	3.99486900	4.05659800
H	-4.82556500	4.12060900	4.39161000
C	-4.10862600	5.50907200	2.88111800
H	-3.88569200	6.31931100	3.58078200
H	-5.09210600	5.71069700	2.44304800
H	-3.37222800	5.55508100	2.07340800
C	7.71016500	-2.44185400	2.85601800
H	8.70186800	-2.17574800	2.47974800
H	7.78952500	-3.42398500	3.33353300
H	7.45403900	-1.71882400	3.63557800
C	-4.64886800	1.68270200	3.28559900
H	-4.08156801	1.52251425	4.17857750
H	-5.68632129	1.76914941	3.53281858

DH3

C	2.66125600	1.17331500	0.93968000
C	3.35682600	0.03220600	1.47513800
H	2.99665100	-0.98251300	1.40270400
C	4.50821300	0.33490600	2.13008800
S	4.80457200	2.06670000	2.12122400
C	3.32543800	2.35992600	1.23316700
C	2.79335700	3.64909200	0.93212700
C	3.50354100	4.83908900	1.16286700
H	4.51245200	4.79292000	1.55635000
C	2.91982700	6.06103500	0.89063000
H	3.46989600	6.97737400	1.07211700
C	1.62456200	6.12515800	0.37968800
H	1.20226600	7.09994700	0.17937200
C	0.87912700	4.97045400	0.12780200
C	1.46452600	3.70201800	0.41106200
C	0.73725500	2.48545300	0.16777600
C	1.36315900	1.22817700	0.30502100
C	0.61247400	0.03369900	0.00177800
C	1.17802000	-1.23601400	-0.38126000
C	0.43619400	-2.41625100	-0.15845900
C	0.99565000	-3.70594500	-0.46303800
C	0.30556500	-4.90212000	-0.11058100
C	0.90283100	-6.13200200	-0.40038800
H	0.40511300	-7.05448700	-0.13607400
C	2.14609400	-6.21113800	-1.02532600
H	2.58066300	-7.18252800	-1.23205500
C	2.82364300	-5.06080100	-1.38000700
H	3.78939400	-5.12572500	-1.86786700
C	2.26565100	-3.80034100	-1.11070500
C	2.89173600	-2.57850000	-1.49958100
C	2.38790900	-1.32579600	-1.16806800
C	3.11889000	-0.27089200	-1.82109900
H	2.86189700	0.77472200	-1.74403400

C	4.14422400	-0.70094300	-2.60275700
S	4.27600000	-2.45388600	-2.56277400
C	5.45750500	-0.60754000	2.81118900
H	4.93964200	-1.56396600	2.93687100
H	5.68268200	-0.24346300	3.82062100
C	6.77788200	-0.84254800	2.05257900
H	6.54743300	-1.21172600	1.04739100
H	7.29686000	0.11353500	1.91792600
C	7.70552700	-1.83151000	2.76670800
H	7.17932600	-2.78367800	2.90543900
H	7.92837100	-1.45735200	3.77333600
C	9.01452100	-2.07814200	2.01157900
H	8.82395200	-2.48525900	1.01390900
H	9.65344900	-2.78813300	2.54356900
H	9.58105500	-1.15004100	1.88738100
C	5.06274400	0.10950900	-3.47207500
H	5.03633900	-0.29104600	-4.49157600
H	4.65444200	1.12223300	-3.53351000
C	6.53346000	0.16151100	-3.00234800
H	7.12871800	0.62604300	-3.79756100
H	6.90675800	-0.86325700	-2.90008900
C	6.76328900	0.92080000	-1.68820100
H	6.11116900	0.50976700	-0.91108000
H	7.79032100	0.73261200	-1.35673500
C	6.54461500	2.43425900	-1.79079700
H	6.76351800	2.92408400	-0.83874500
H	5.51200000	2.68393600	-2.04840400
H	7.19505300	2.87677300	-2.55255400
C	-2.70723200	1.41603500	-0.92834900
C	-3.55207100	0.32772000	-1.35103000
H	-3.31534200	-0.70999100	-1.18353100
C	-4.67468000	0.71462300	-2.01080400
S	-4.74869000	2.46438800	-2.16047500
C	-3.22481300	2.64605500	-1.31984500
C	-2.53886300	3.88187100	-1.13137800
C	-3.10198800	5.12423600	-1.46856100
H	-4.11013400	5.16531000	-1.86447900
C	-2.37527500	6.28604000	-1.29764500
H	-2.81158400	7.24284500	-1.56087400
C	-1.07989300	6.23735500	-0.78480700
H	-0.54272700	7.16792500	-0.66572500
C	-0.47720400	5.02762900	-0.43085700
C	-1.21142600	3.81820900	-0.60929300
C	-0.63447500	2.54759600	-0.26231200
C	-1.40505600	1.36351300	-0.30131800
C	-0.79391100	0.11458000	0.09208300
C	-1.48925600	-1.05996400	0.56205600
C	-0.87414100	-2.32532300	0.42778200
C	-1.56116800	-3.52638100	0.82096000
C	-0.99903000	-4.80995600	0.55656200
C	-1.71909100	-5.94780100	0.93005600
H	-1.31972000	-6.93287900	0.73337000
C	-2.96165300	-5.85451800	1.55454500
H	-3.49291300	-6.75900900	1.82806700

C	-3.51591700	-4.61840000	1.82423200
H	-4.48123500	-4.54844700	2.31228200
C	-2.83188800	-3.44437200	1.46782900
C	-3.33091300	-2.14013200	1.75989900
C	-2.70303900	-0.97115000	1.34309000
C	-3.33836800	0.19664700	1.89711600
H	-2.98395000	1.20440700	1.74171100
C	-4.41430400	-0.07121100	2.68302300
S	-4.71143300	-1.80135300	2.77933200
C	-5.77880100	-0.12638800	-2.59063200
H	-5.90360700	0.12564200	-3.65123100
H	-6.72605100	0.14660800	-2.10807300
C	-5.56505900	-1.63879400	-2.45404700
H	-4.63314500	-1.92198400	-2.95640300
H	-5.43910100	-1.89697100	-1.39676700
C	-6.72440800	-2.45350000	-3.03902100
H	-6.85759600	-2.18918000	-4.09508400
H	-7.65591300	-2.17053100	-2.53401400
C	-6.51523100	-3.96515200	-2.91386600
H	-5.61221900	-4.28438900	-3.44301600
H	-7.35940800	-4.51955900	-3.33254300
H	-6.40628400	-4.26376700	-1.86688100
C	-5.27791100	0.88792300	3.45071300
H	-5.28682000	0.59681500	4.50711000
H	-4.80117400	1.87141300	3.41048600
C	-6.73841700	0.98568800	2.95592900
H	-7.30785800	1.57124600	3.68753400
H	-7.17818900	-0.01750300	2.95849300
C	-6.90763900	1.61304500	1.56458400
H	-6.27374800	1.08320800	0.84547100
H	-7.94166600	1.45437100	1.23902700
C	-6.59632400	3.11290100	1.51497600
H	-6.76904300	3.51419500	0.51357500
H	-5.55425200	3.32371400	1.76889100
H	-7.22932100	3.66969700	2.21381200

3. Snapshots of MD-equilibrated systems

Snapshots of MD simulations performed for the DH systems are represented here. The snapshots are taken from the final time step of MD run.

DH1

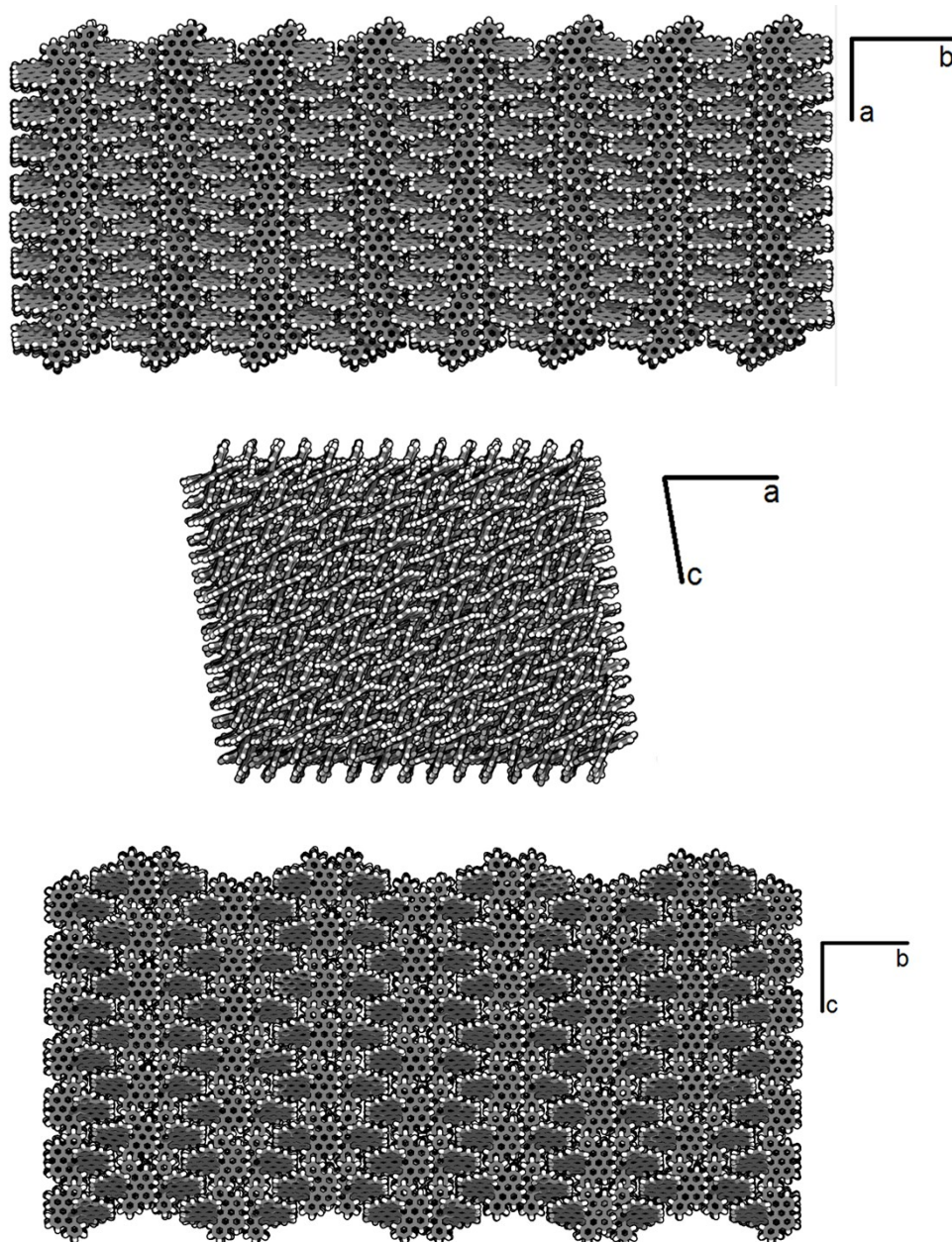


Figure S1. Snapshots of three planes of MD-equilibrated **DH1** system.

DH2

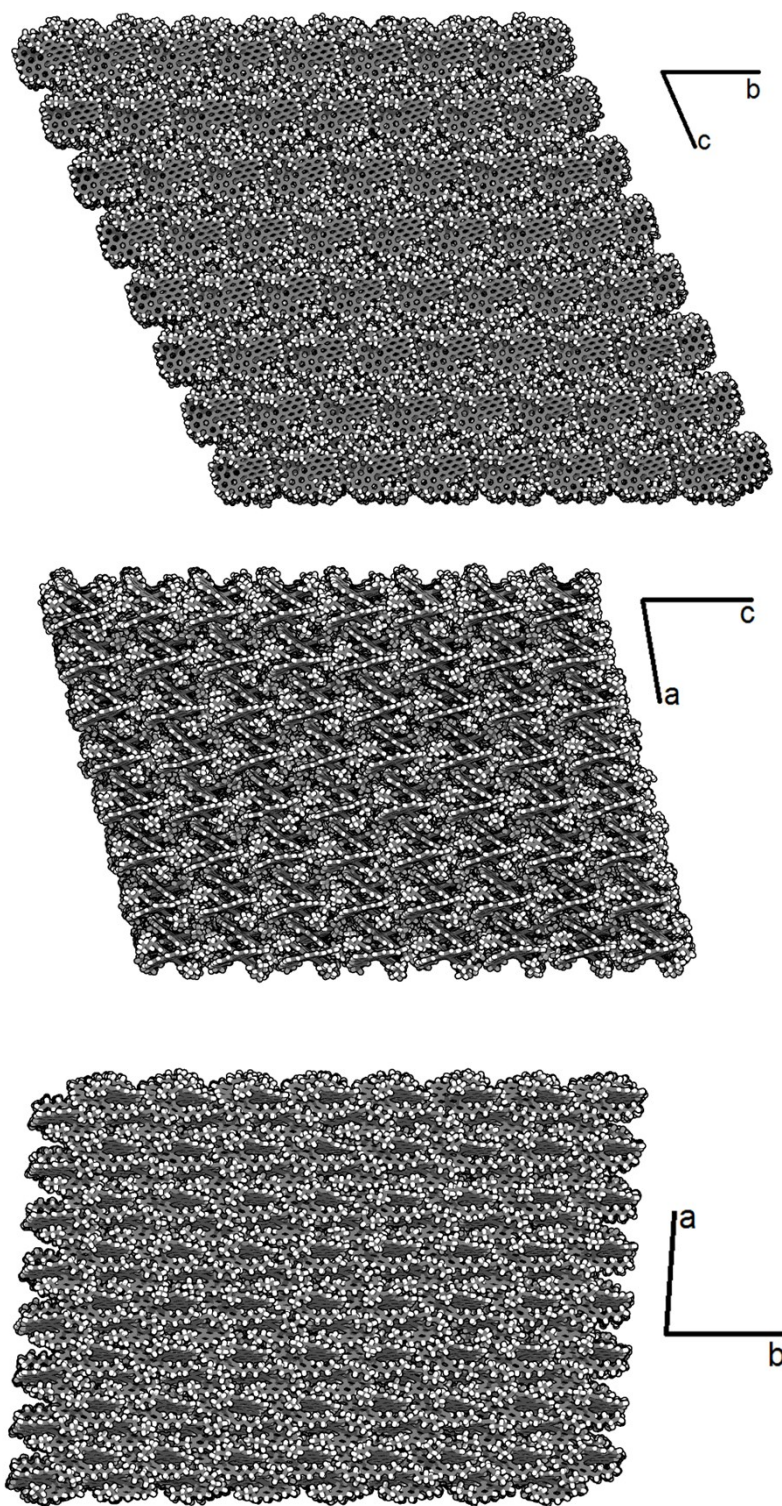


Figure S2. Snapshots of three planes of MD-equilibrated **DH2** system.

DH3

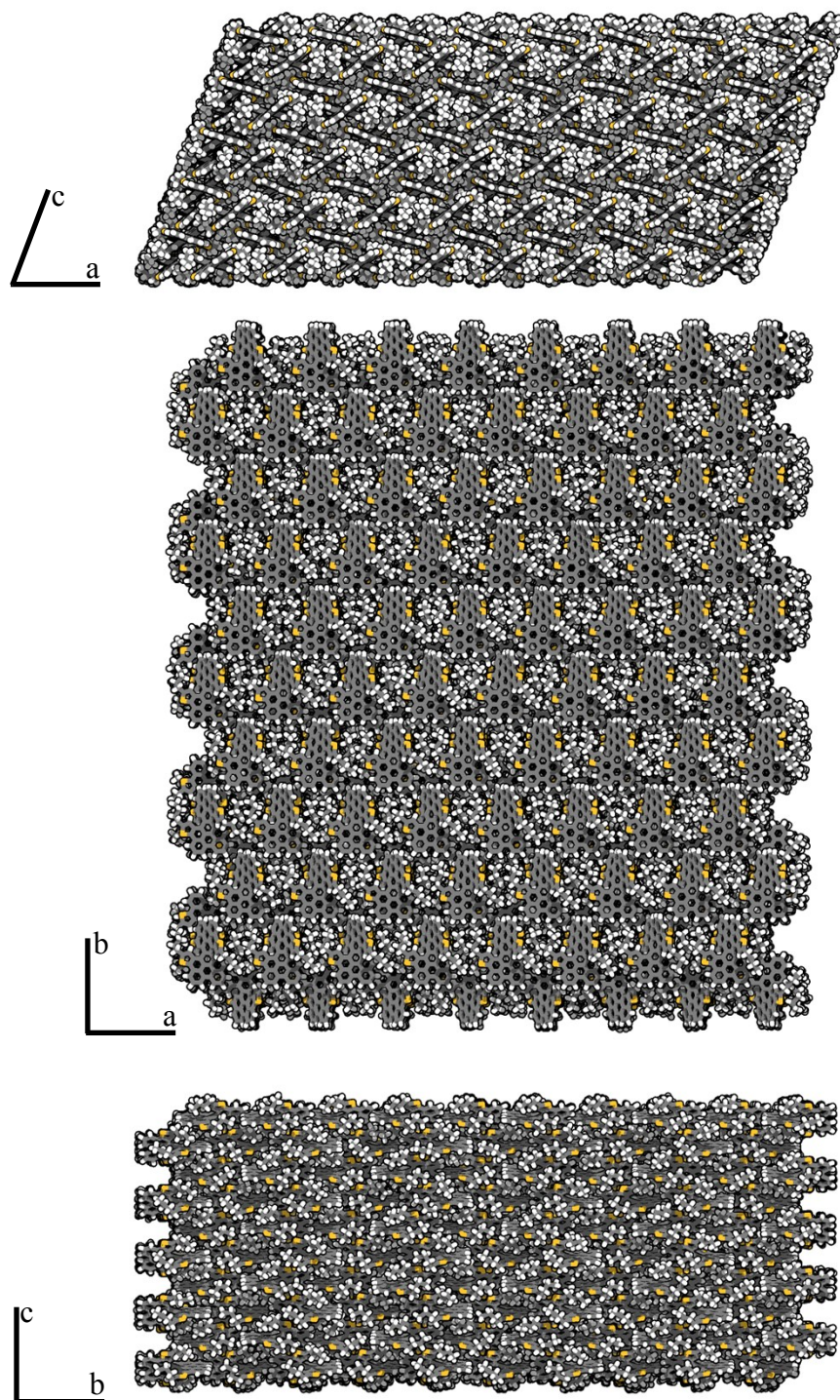


Figure S3. Snapshots of three planes of MD-equilibrated **DH3** system.

4. Measured distances and electronic coupling between residues

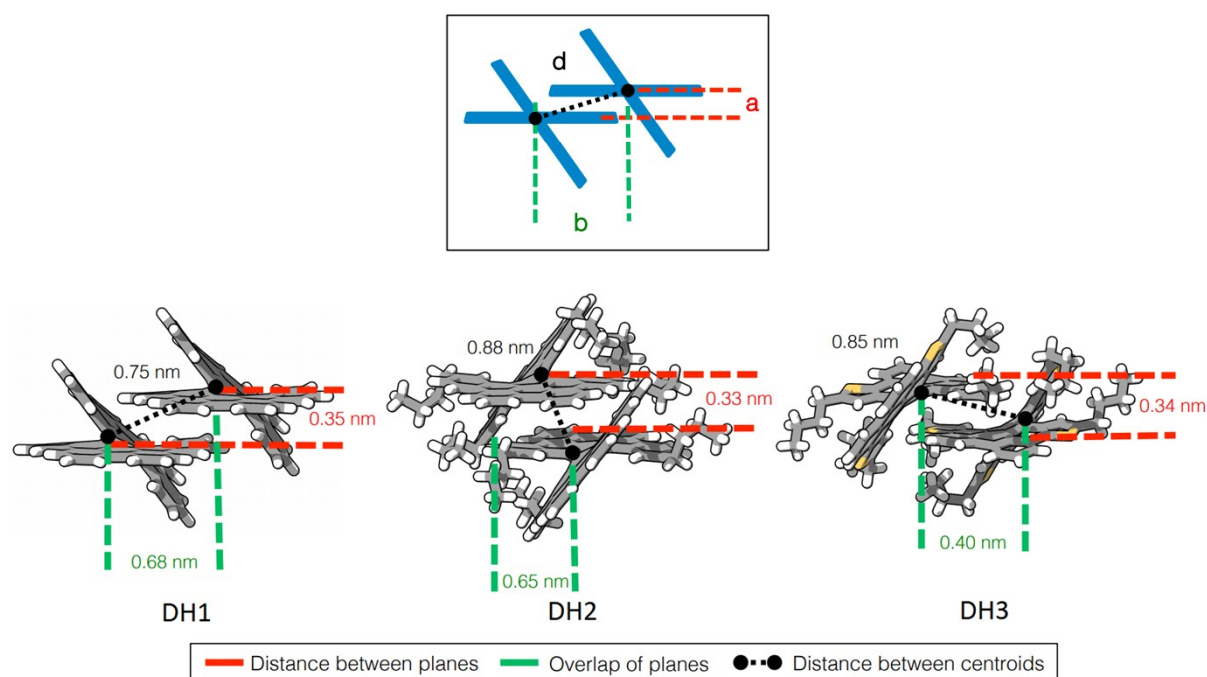


Figure S4. Measured distances and electronic coupling between adjacent residues.

Table 1. Distances between adjacent DH molecules

	a (nm)	b (nm)	d (nm)	J(meV)
DH1	0.35	0.68	0.75	58
DH2	0.33	0.65	0.88	73
DH3	0.34	0.40	0.85	37

5. References

- (S1) Fratini, S. Ciuchi, S. Mayou, D. Trambly de Laissardière, G. and Troisi, A. A Map of High-Mobility Molecular Semiconductors. *Nature Mat.* 2017, 16, 998-1002.
- (S2) Becke, A. D. *J. Chem. Phys.* 1993, 98, 5648–5652.
- (S3) Lee, C. Yang, W. and Parr, R. G. *Phys. Rev. B* 1988, 37, 785–789.
- (S4) Stephens, P. J. Devlin, F. J. Chabalowski, C. F. and Frisch, M. J. *J. Phys. Chem.* 1994, 98, 11623–11627.
- (S5) Vosko, S. H. Wilk, L. and Nusair, M. *Can. J. Phys.* 1980, 58, 1200–1211.
- (S6) Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. Scalmani, G. Barone, V. Mennucci, B. Petersson, G. A. Nakatsuji, H. Caricato, M. Li, X. Hratchian, H. P. Izmaylov, A. F. Bloino, J. Zheng, G. Sonnenberg, J. L. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M. Nakajima, T. Honda, Y. Kitao, O. Nakai, H. Vreven, T. Montgomery, J. A., Jr. Peralta, J. E. Ogliaro, F. Bearpark, M. Heyd, J. J. Brothers, E. Kudin, K. N. Staroverov, V. N. Kobayashi, R. Normand, J. Raghavachari, K. Rendell, A. Burant, J. C. Iyengar, S. S. Tomasi, J. Cossi, M. Rega, N. Millam, N. J. Klene, M. Knox, J. E. Cross, J. B. Bakken, V. Adamo, C. Jaramillo, J. Gomperts, R. Stratmann, R. E. Yazyev, O. Austin, A. J. Cammi, R. Pomelli, C. Ochterski, J. W. Martin, R. L. Morokuma, K. Zakrzewski, V. G. Voth, G. A. Salvador, P. Dannenberg, J. J. Dapprich, S. Daniels, A. D. Farkas, Ö. Foresman, J. B. Ortiz, J. V. Cioslowski, J. and Fox, D. J. *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford, CT, 2009.