

SUPPLEMENTARY INFORMATION

Polydopamine and eumelanin models in various oxidation states

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SUPPLEMENTARY FIGURES

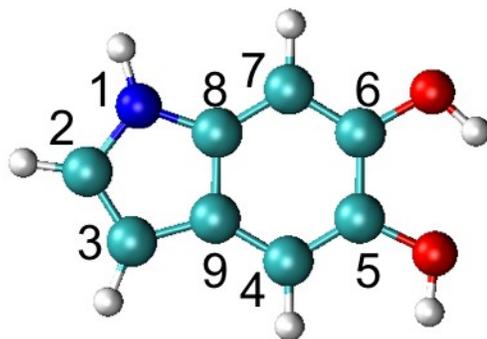


Figure S1 | Molecular structure of DHI monomer. Atoms in the DHI monomer are numbered in the standard notation. The same notation is used in our previous study.¹

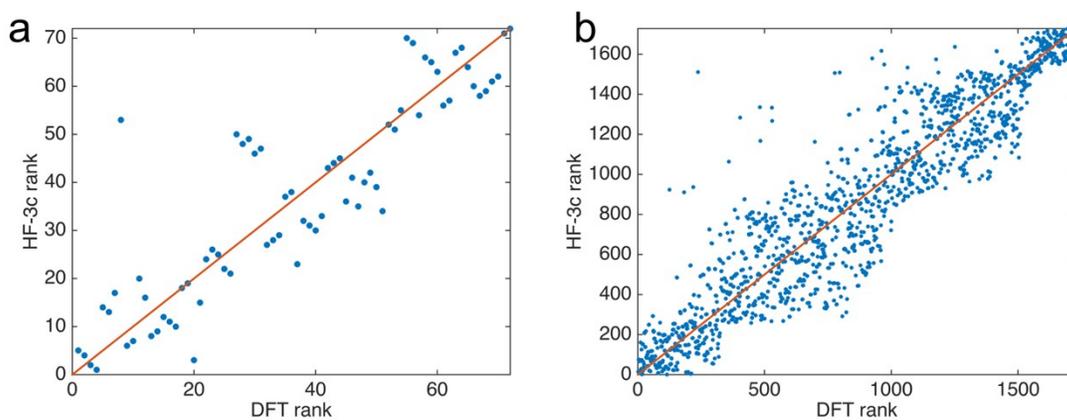


Figure S2 | Comparison of results for dimers and trimers using HF-3c method and BLYP/def2-SVP/SMD/gCP method. (a) The DFT rank against the HF-3c rank for the 72 dimers. (b) The DFT rank against the HF-3c rank for the 1,728 trimers. The results show that the HF-3c method produces a similar rank as the BLYP/def2-SVP/SMD/gCP method produces, suggesting that the HF-3c method can be used as a filter to screen out molecular structures that are much less stable, thus reducing the number of molecular structures for more computationally expensive DFT calculations.

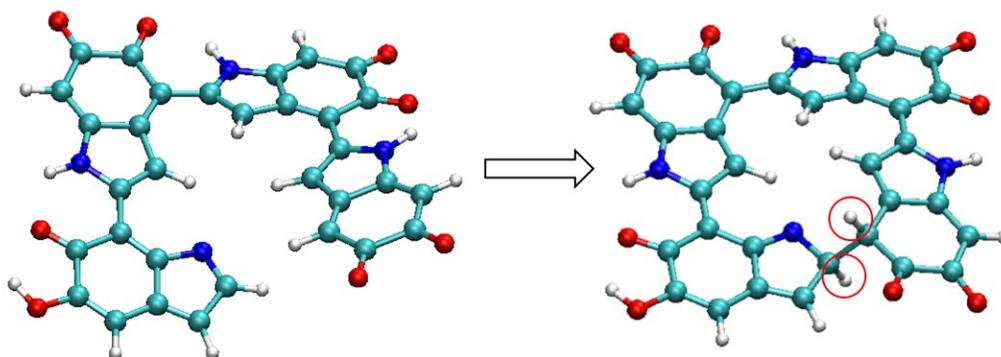


Figure S3 | Formation of new covalent bond. In the most stable tetramer, which is made of the 2,4' & 2,4' & 2,7' position with three IQs and one MQ, there is a new covalent bond formed between the first and fourth monomers during the DFT geometry optimization, making the molecular structure cyclic. The non-cyclic tetramer at the left of the figure is the molecular structure before the DFT geometry optimization. The cyclic tetramer at the right of the figure is the molecular structure after the DFT geometry optimization. The hydrogen atoms that are circled become less stable when the new covalent bond is formed. Since there is no kinetic energy in our static DFT calculations and there are no other molecules (e.g., water molecules, ions) in the simulation, these two hydrogen atoms are still attached to the first and fourth monomers.

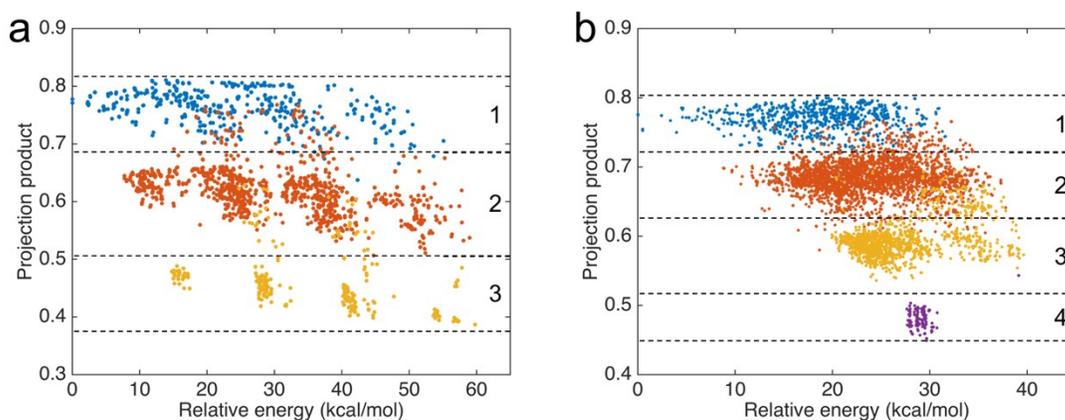


Figure S4 | Additional statistical characteristics of data for trimers and tetramers. (a) The projection products against the relative energies of the 1,720 trimers. Blue represents the trimers having two favorable connections, red represents the trimers having one favorable connection and one unfavorable connection, and yellow represents the trimers having two unfavorable connections. These results can be separated into three regions. (b) The projection products against the relative energies of the top 5,184 tetramers. Blue represents the tetramers having three favorable connections, red represents the tetramers having two favorable connections and one unfavorable connection, and yellow represents the tetramers having one favorable connection and two unfavorable connections, and purple represents the tetramers having three unfavorable connections. These results can be separated into four regions.

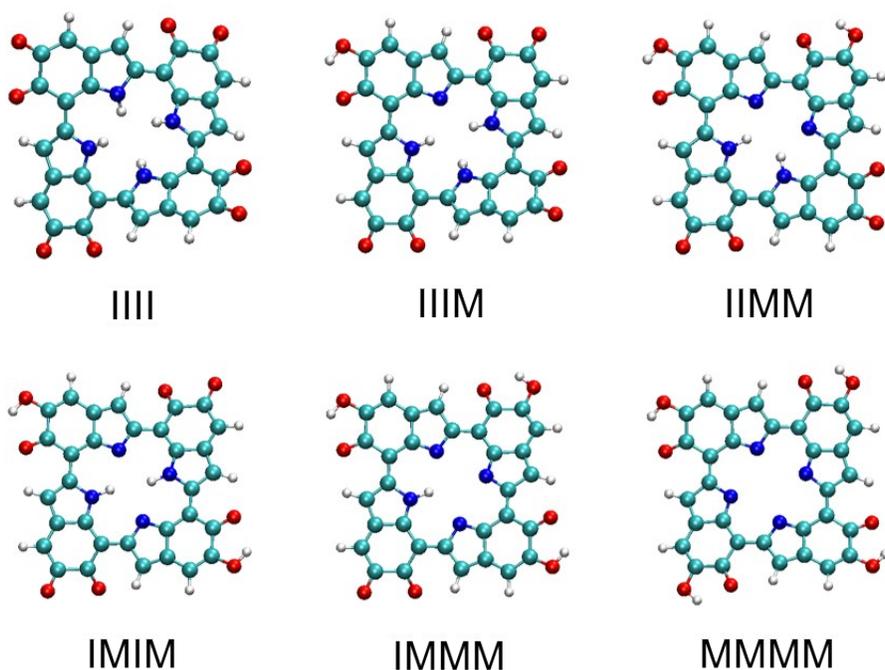


Figure S5 | Molecular structures of porphyrin-like tetramers. These porphyrin-like tetramers were first proposed by Kaxiras et al. in 2006.² In these porphyrin-like tetramers, the connections are all 2,7' connections with the four nitrogen atoms in the center. The abbreviation of each tetramer represents the type and the order of monomers in each tetramer. For example, the IMIM tetramer consists of two IQs and two MQs in the order of IQ-MQ-IQ-MQ.

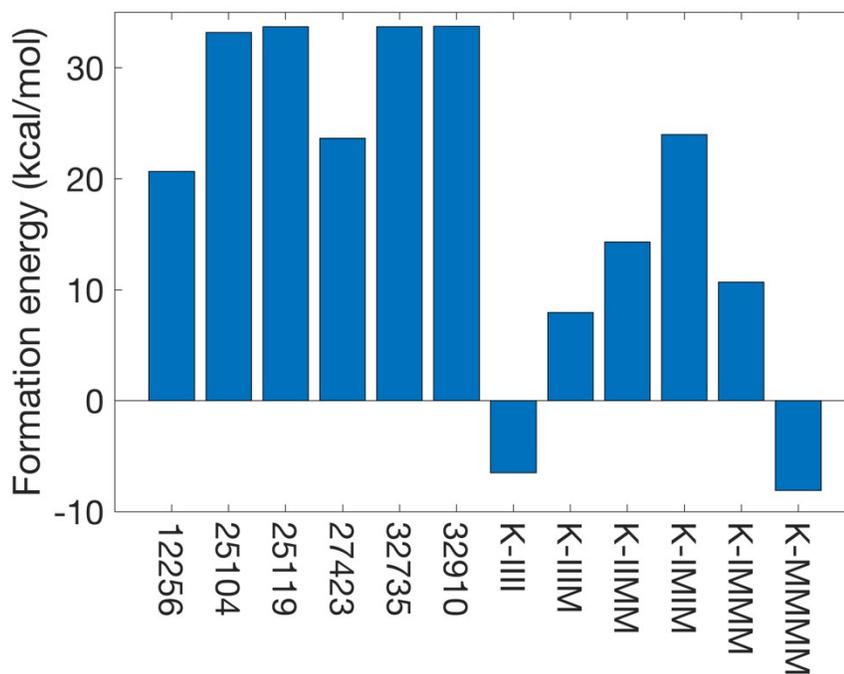


Figure S6 | Formation energies of cyclic tetramers in gas phase. The comparison of formation energies (in the gas phase) of the cyclic tetramers proposed in this work and those porphyrin-like tetramers proposed by Kaxiras et al. in 2006.² The formation energy of a tetramer is defined as the difference between the ground state energy of the four isolated monomers and the summation of the ground state energy of the tetramer and the ground state energy of four isolated hydrogen molecules.

SUPPLEMENTARY METHODS

Brute-force algorithmic generator

DHI oligomers are composed of various numbers of DHI units with different configurations. In this work, we use multi-layers of checkerboard plates to represent different polymerization degrees of DHI oligomers. For example, a tetramer can be generated with four layers of checkerboard plates (Fig. S7). We consider eight different orientations of a DHI monomer to generate DHI oligomers. Orientation 1 is the default orientation. Orientation 2 is a flipped structure of orientation 1. Orientation 3 is a 90-degree clockwise-rotated structure of orientation 1. Orientation 4 is a flipped structure of orientation 3. Similarly, orientation 5 is a 180-degree clockwise-rotated structure of orientation 1. Orientation 6 is a flipped structure of orientation 5. Orientation 7 is a 270-degree clockwise-rotated structure of orientation 1. Orientation 8 is a flipped structure of orientation 7. With these eight different orientations, we can generate all probable DHI oligomers by assembling two or more DHI monomers with different orientations on checkerboard plates. Finding the lowest energy conformation of an oligomer is critical for comparing its energy with other oligomers. Note that the brute-force algorithmic generator not only can generate all probable structural unique oligomers but also can generate all different conformations. Consequently, the conformational analysis is done at the same time while we evaluate the energies of different conformations of oligomers. A total of 18 reduced dimers, 216 reduced trimers, and 2,592 reduced tetramers are systematically generated. To find the most stable configurations of those oligomers, their molecular structures are equilibrated in MD simulations and then optimized using DFT calculations. The details of the brute-force algorithmic generator are available in our previous study.¹

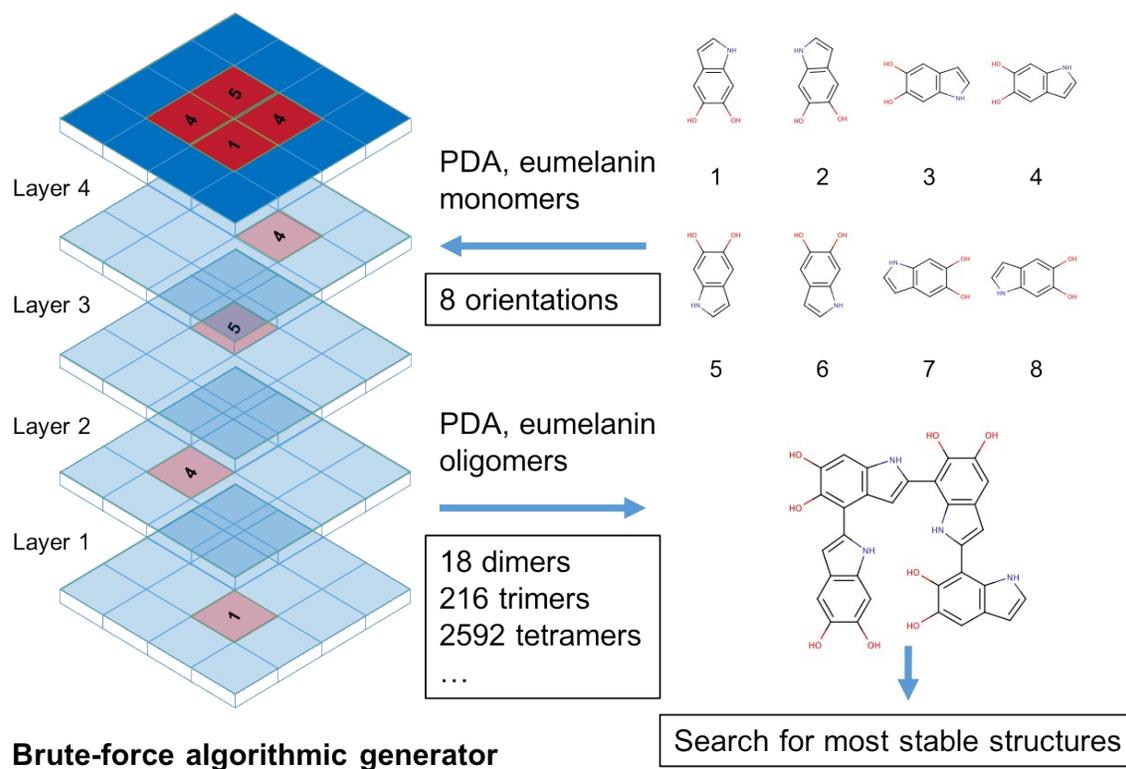


Figure S7 | Brute-force algorithmic generator using multi-layers of checkerboard plates to generate different DHI oligomers. Four layers of checkerboard plates are used to generate a DHI tetramer. The red blocks represent the elements that are occupied for generating a DHI tetramer and the blue blocks represent the available elements. The numbers on the red blocks represent the orientation of DHI monomers. Eight different orientations of a DHI monomer are considered in the algorithm. The molecular structure of a tetramer that is generated according to the four layers of checkerboard plates.

Method used to calculate the projection product.

1. Locate the coordinates of four reference atoms in each DHI monomer. The four reference atoms in a DHI monomer are shown in Fig. S8.
2. Generate the reference vectors, $Vector\ 13_i$ and $Vector\ 24_i$, for the i -th DHI monomer.
3. Define the orientation vector, $Vector\ n_i = Vector\ 13_i \times Vector\ 24_i$, for the i -th DHI monomer.
4. Normalize $Vector\ n_i$ to a unit vector.
5. The projection product of an oligomer made of m DHI monomers is defined as:

$$Projection\ product = \sum_{i=1}^{m-1} |Vector\ n_i \cdot Vector\ n_{i+1}| / (m-1)$$

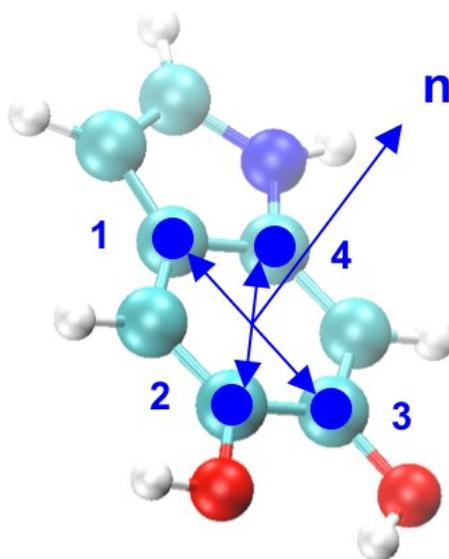


Figure S8 | Definition of orientation vector for DHI monomer. The numbers indicate the four reference atoms used to define the orientation vector for a DHI monomer.

SUPPLEMENTARY REFERENCES

1. C.-T. Chen, F. J. Martin-Martinez, G. S. Jung and M. J. Buehler, *Chemical Science*, 2017.
2. E. Kaxiras, A. Tsolakidis, G. Zonios and S. Meng, *Physical review letters*, 2006, **97**, 218102.