

## Electronic Supplementary Information

### Charge transfer in DHICA eumelanin-like oligomers: Role of hydrogen bonds

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**Computational Details** - All the oligomeric structures (dimers, trimers and tetramers) are generated using combinatorial algorithms (all possible combinations of DHICA monomer units).

We have sorted the unique ones from all possible structures using K-Means clustering algorithm, where we have taken inertia as the evaluation metric to obtain the optimum number of clusters for each set of dimers, trimers and tetramers.

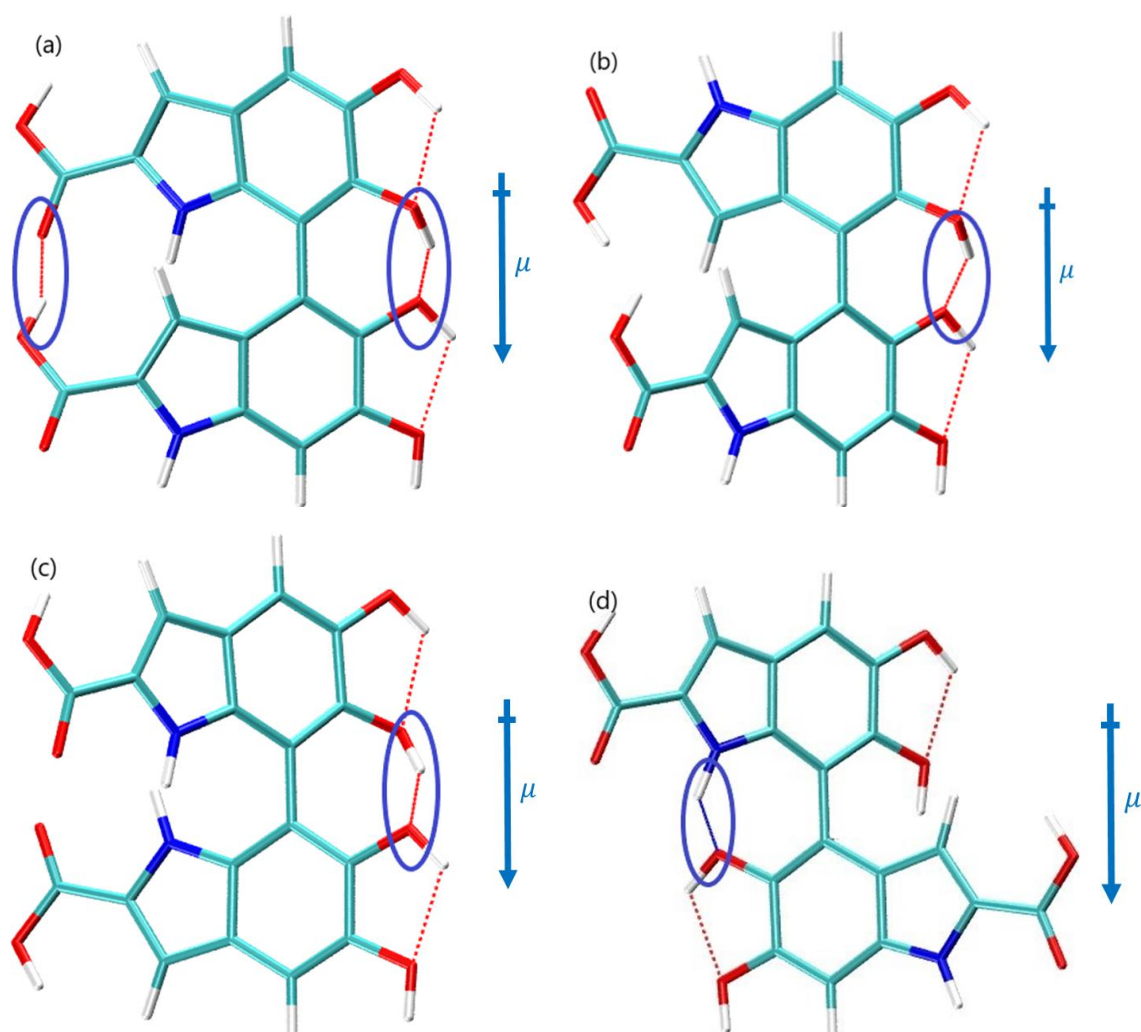
From the features in these oligomers, the most stable forms of pentamers and octamers are created. The relative stability of the isomers are calculated within  $\omega$ B97X-D/6-31G\*, B3LYP/6-31G\* and MP2/6-31G\* levels of theory. The structures and energies obtained via these three methods are comparable and included below. Ionization energies are calculated by taking difference in energies at  $\omega$ B97X-D/6-31G\* level of theory. Constrained density functional theory configuration interaction (CDFT-CI) at B3LYP/6-31G\* level is used to compute the charge transfer coupling matrix elements ( $V_{12}$ ) between the neutral species vs charge separated species. Q-Chem[1] quantum chemistry software package is used for these calculations.

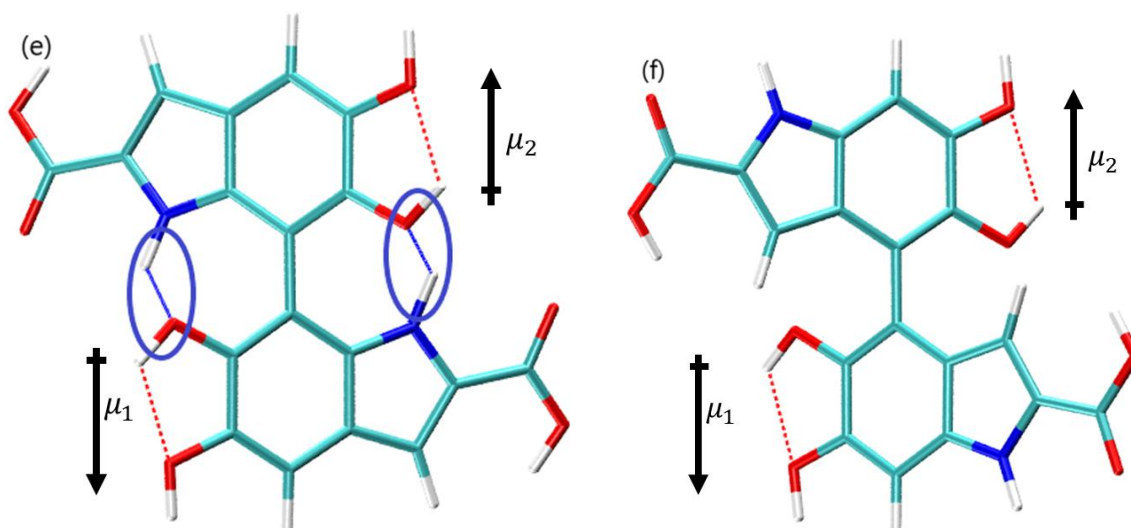
The pentamer and octamer structures are used to initiate ab initio molecular dynamics simulations with constant NVT, 0.5fs time step and 300K temperature for a total of 50ps. This is done with the DFTB+ software package.[2]

**Table S1** Comparison of relative energies of DHICA dimers obtained with different level of theories and 6-31G\* basis set.

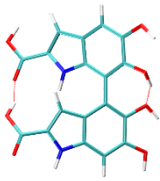
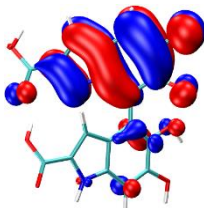
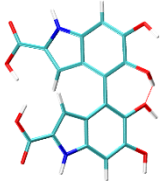
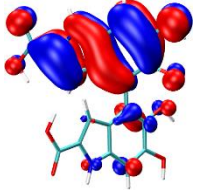
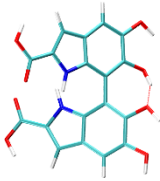
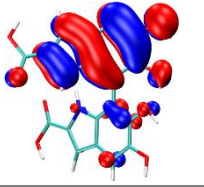
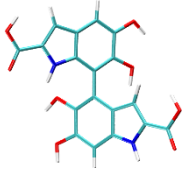
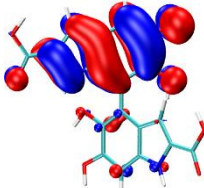
Species	Rel. energy (kcal/mol)		
	$\omega$ B97X-D	B3LYP	MP2
4-7' cis	0	0.006	0
4-4' cis	0.63	0	1.36
7-7' cis	0.97	0.19	1.39
4-7' trans	4.01	2.95	4.49
7-7' trans	4.85	3.22	4.83
4-4' trans	8.40	7.08	9.05

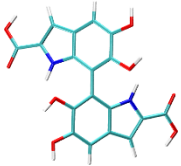
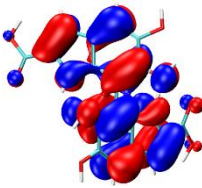
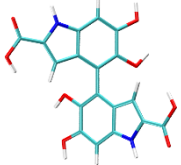
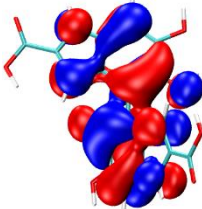
**Fig. S1** Identification of inter-monomer H-bonds (blue ellipse), resultant dipole (blue arrow) and local dipole (black arrow) in (a) 4-7' cis, (b) 4-4' cis, (c) 7-7' cis, (d) 4-7' trans, (e) 7-7' trans and (f) 4-4' trans dimers.





**Table S2** Ionization energies and coupling matrix elements of stable dimers.

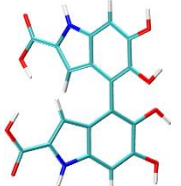
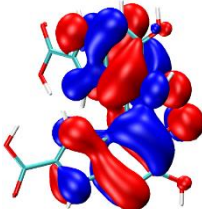
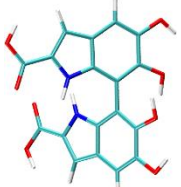
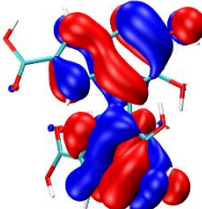
	Species	Rel. energy (kcal/mol)	VIE (eV)	Koopmans' IE (eV)	HOMO	$V_{12}$ (a.u.)
	4-7' cis	0	7.55	7.94		0.147
	4-4' cis	0.63	7.40	7.84		0.112*
	7-7' cis	0.97	7.42	7.89		0.120
	4-7' trans	4.01	7.47	7.86		0.115

	7-7' trans	4.85	7.34	7.78		0.106
	4-4' trans	8.40	7.32	7.94		0.099

\*Due to convergence issues, a smaller 6-31G basis was used

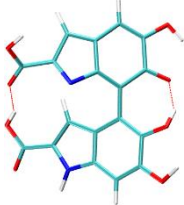

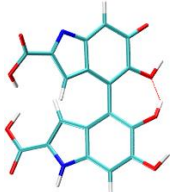
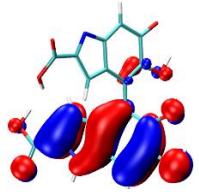
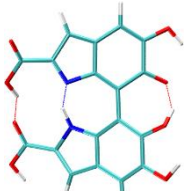

The last structure in Table S2 does not have H-bonds or favourable charge-dipole interactions between monomers and we notice that the coupling is significantly lower.

**Table S3** Ionization energies and coupling matrix elements of OH rotated dimers.

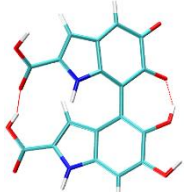

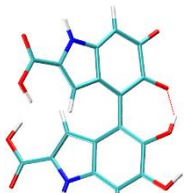

	Species	Rel. energy (kcal/mol)	VIE (eV)	Koopmans' IE (eV)	HOMO	V <sub>12</sub> (a.u.)
	4-4' cis	8.31	7.26	7.89		0.103
	7-7' cis	2.11	7.92	8.27		0.118

In Table S3, the rotamers are OH rotated forms of 4-4' cis and 7-7' cis structures and for both these forms the coupling is lower than when the H-bonding interactions are most favourable.

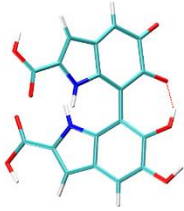
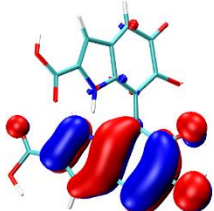
**Table S4** Ionization energies and coupling matrix elements of cis DHICA-MKICA dimers.

	<b>Species</b>	<b>Rel. energy (kcal/mol)</b>	<b>VIE (eV)</b>	<b>Koopmans' IE (eV)</b>	<b>HOMO</b>	<b>V<sub>12</sub> (a.u.)</b>
	4-7' cis	8.66	7.38	7.75		0.075
	4-4' cis	9.52	7.85	8.27		0.099
	7-7' cis	0	7.69	8.14		0.080

**Table S5** Ionization energies and coupling matrix elements of cis DHICA-DKICA dimers.

	<b>Species</b>	<b>Rel. energy (kcal/mol)</b>	<b>VIE (eV)</b>	<b>Koopmans' IE (eV)</b>	<b>HOMO</b>	<b>V<sub>12</sub> (a.u.)</b>
	4-7' cis	0	7.53	7.92		0.084
	4-4' cis	1.43	7.71	8.19		0.068

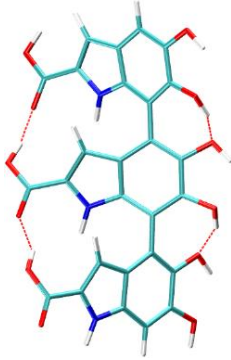
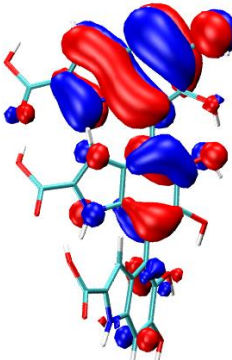
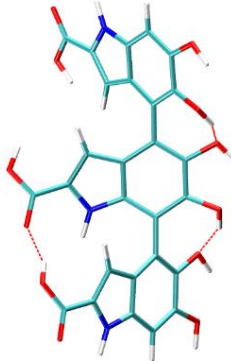
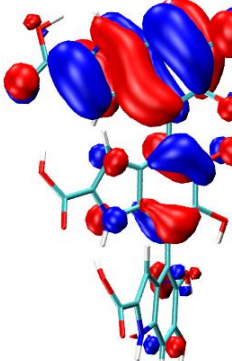
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	7-7' cis	1.31	7.67	8.05		0.069
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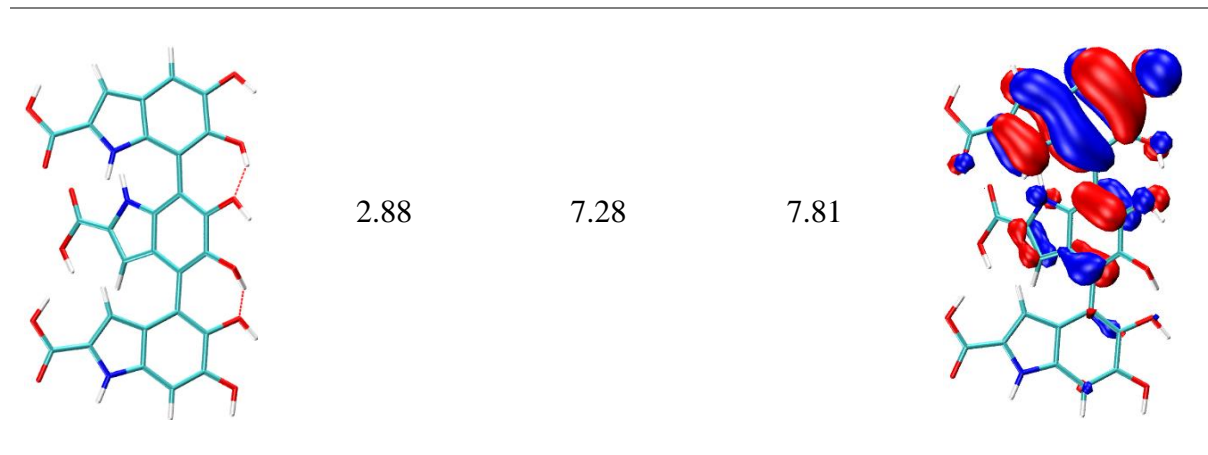
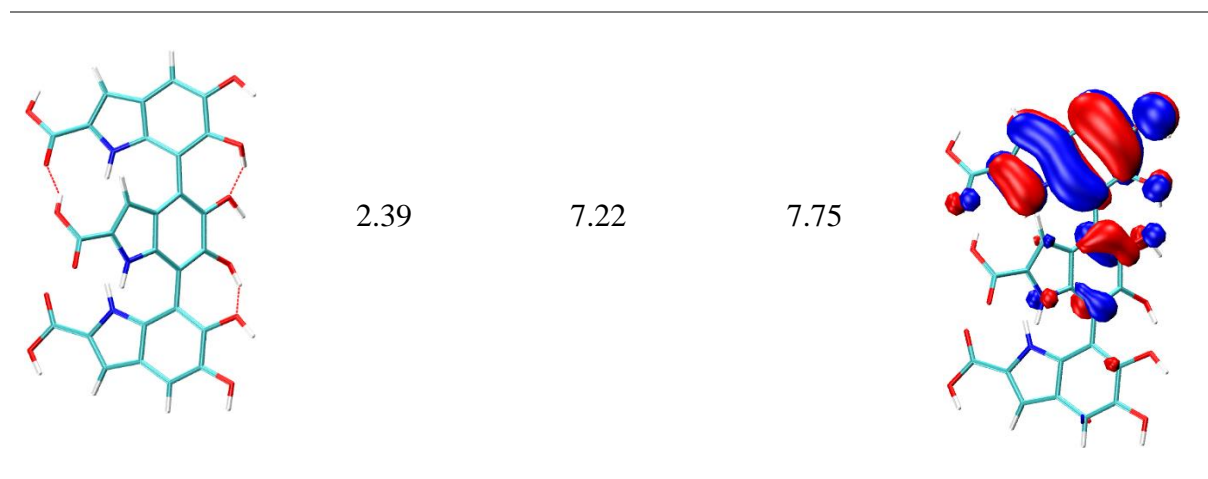
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In Table S4 and S5, the DHICA-MKICA and DHICA-DKICA dimers have significantly lower charge transfer coupling due to charge localization on one or the other monomer which does not allow facile charge transfer. This is due to difference in ionization energies and electron affinities between the moieties.

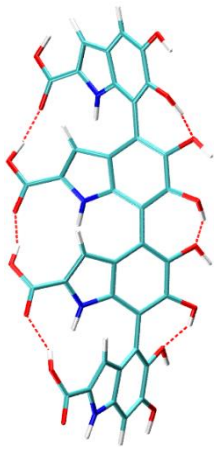
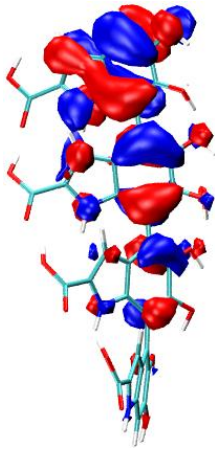
**Table S6** Relative energies and ionization energies of all-cis trimers.

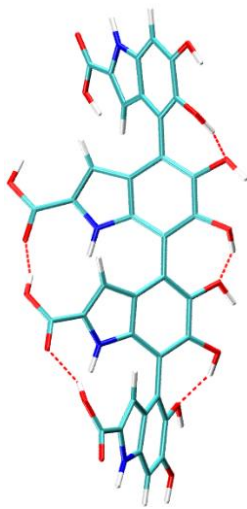
	<b>Rel. energy (kcal/mol)</b>	<b>VIE (eV)</b>	<b>Koopmans' IE (eV)</b>	<b>HOMO</b>
	0	7.25	7.81	
	1.42	7.30	7.81	

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**Table S7** Relative energies and ionization energies of all-cis tetramers.

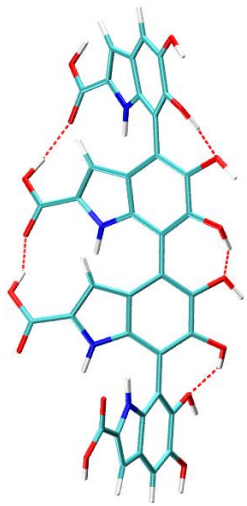
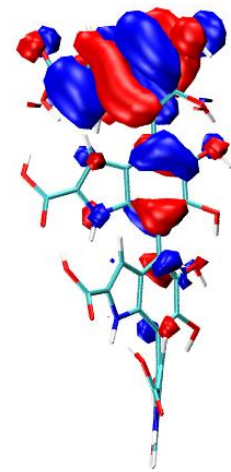
	<b>Rel. energy (kcal/mol)</b>	<b>VIE (eV)</b>	<b>Koopmans' IE (eV)</b>	<b>HOMO</b>
	0	7.16	7.73	



1.01

7.22

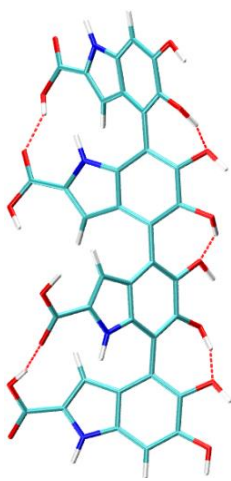
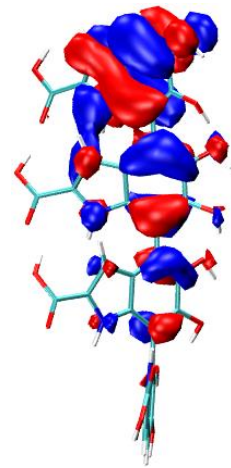
7.75



1.66

7.13

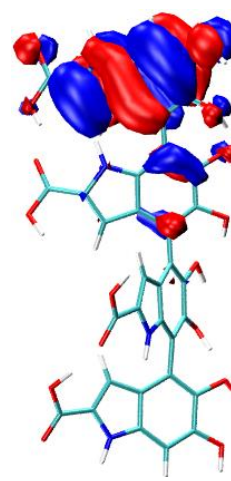
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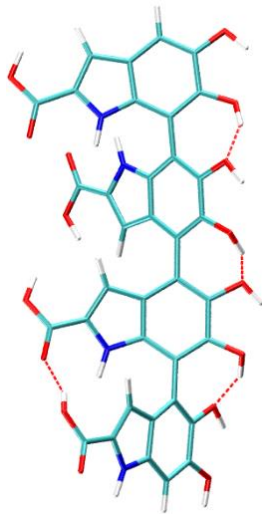
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7.14

7.62



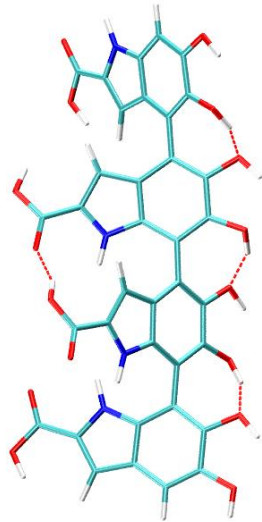
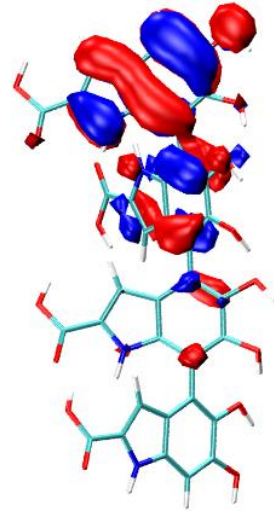




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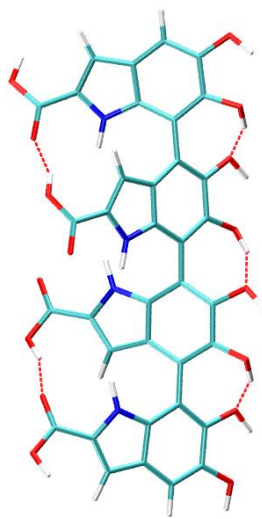
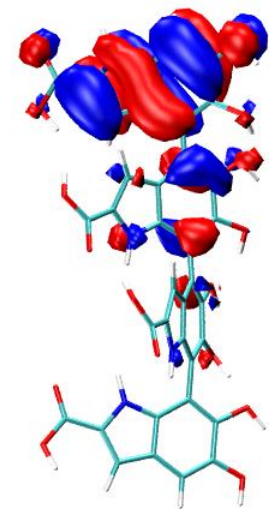
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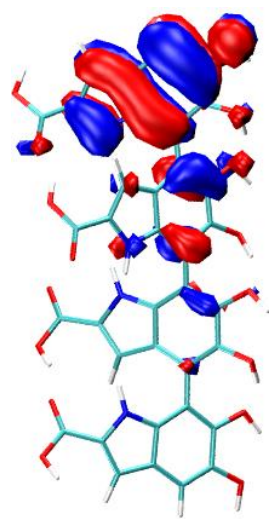
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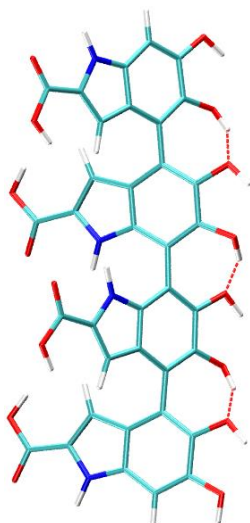


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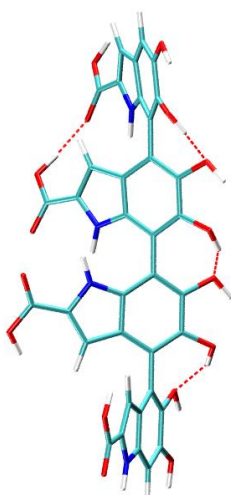
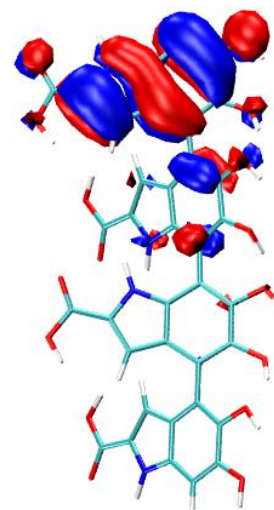




4.11

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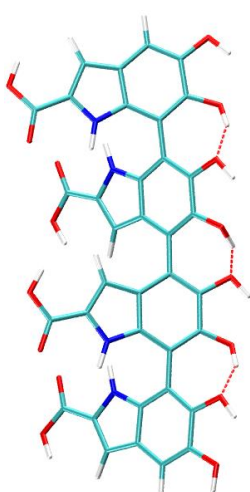
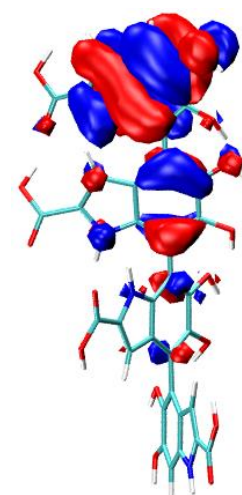
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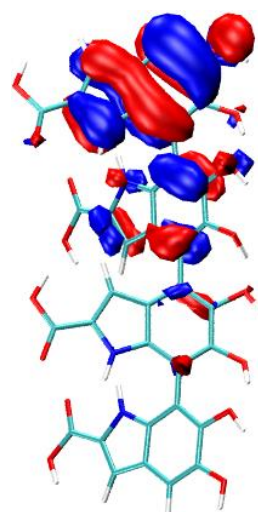
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4.45

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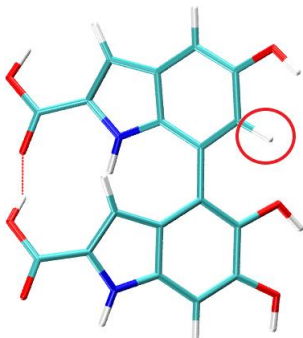


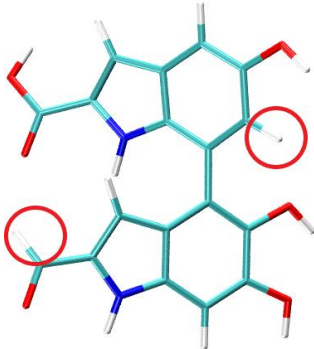
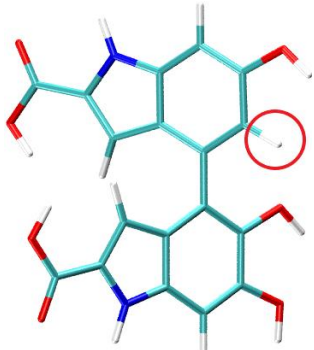
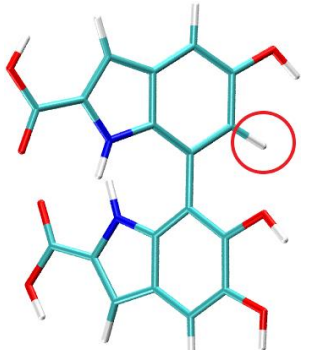
**Table S8** Coupling matrix elements of 4-7', 4-4' and 7-7' isomers of dimer at different inter-monomer angles.

4-7'		4-4'		7-7'	
Angle (Deg.)	V <sub>12</sub> (a.u.)	Angle (Deg.)	V <sub>12</sub> (a.u.)	Angle (Deg.)	V <sub>12</sub> (a.u.)
10	0.150	10	0.131	10	0.136
30	0.126	30	0.131	25	0.136
50	0.116	50	0.116	50	0.120
70	0.114	75	0.115	70	0.114
90	0.141	95	0.111	90	0.142
110	0.118	115	0.113	110	0.110
140	0.120	130	0.116	140	0.111
160	0.131	150	0.117	160	0.136
180	0.131	180	0.131	180	0.137

In Table S8, we notice that with rotation, as the H-bonds become weaker the coupling decreases for all the isomers, 4-4', 4-7' and 7-7' structures.

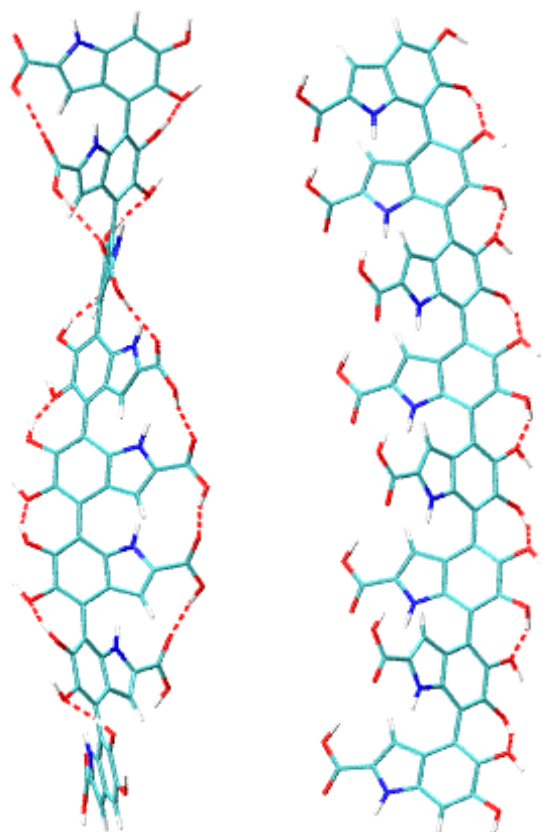
**Table S9** Comparison of dipole moments and coupling matrix elements between stable dimers with inter-monomer H-bonding and dimers without inter-monomer H-bonding.

Species	Dipole moment without H-bonding (Debye)	Dipole moment with H-bonding (Debye)	V <sub>12</sub> without H-bonding (a.u.)	V <sub>12</sub> with H-bonding (a.u.)
 4-7' cis	<b>6.80</b>	7.57	<b>0.137</b>	0.147

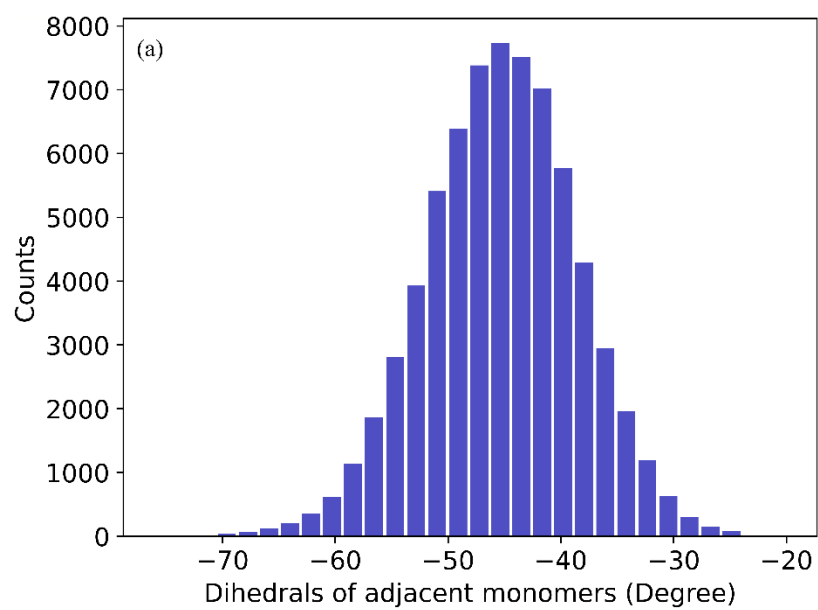
	4-7' cis	<b>5.42</b>	7.57	<b>0.121</b>	0.147
	4-4' cis	<b>7.91</b>	8.54	<b>0.106</b>	0.112*
	7-7' cis	<b>7.10</b>	7.78	<b>0.105</b>	0.120

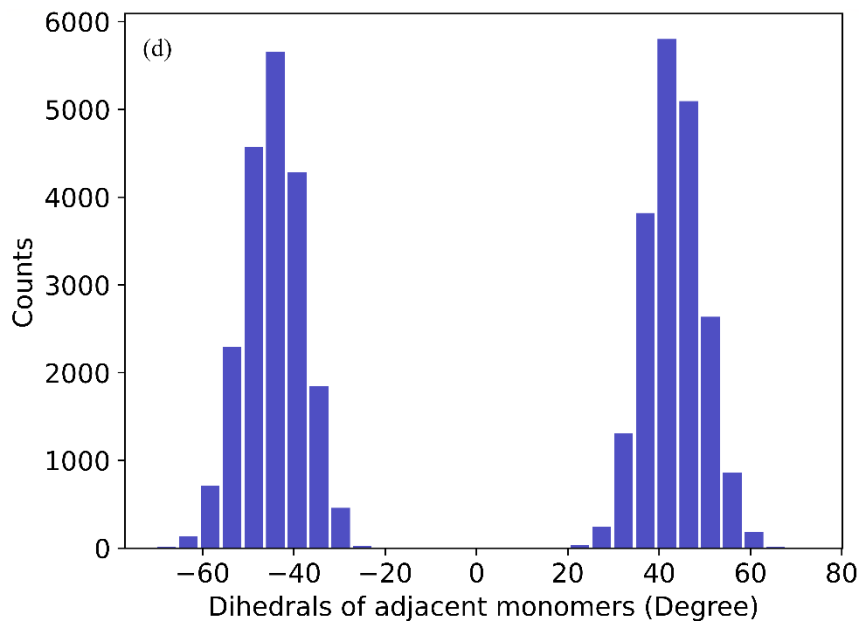
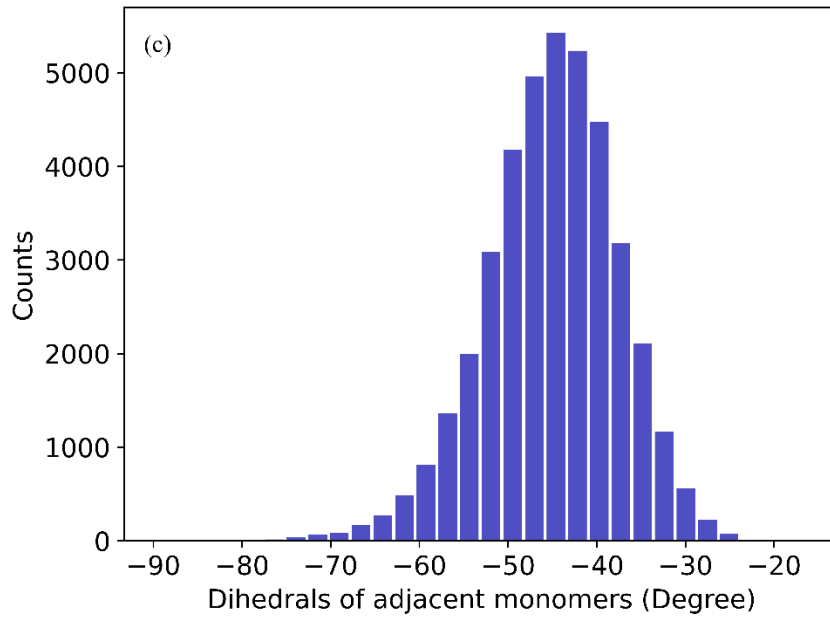
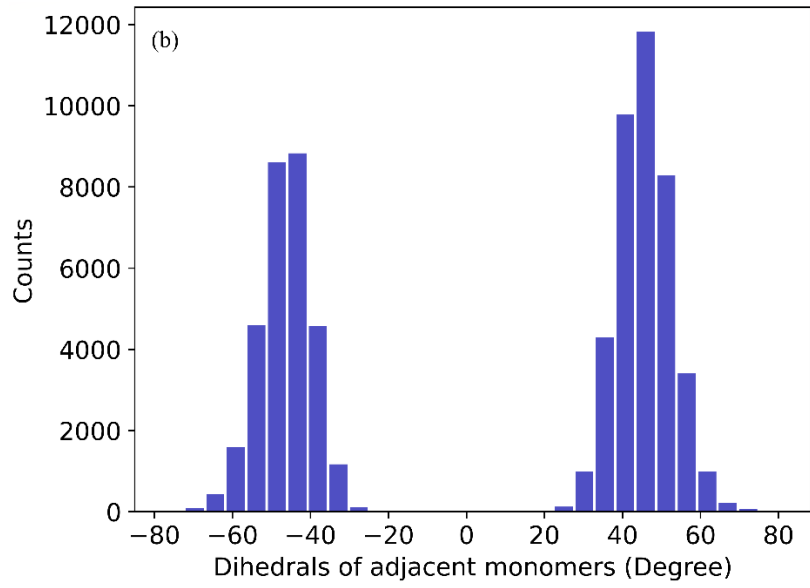
In Table S9, structures represent where one of the -OH groups are replaced by -H (marked by red circle) to destroy inter-monomer H-bonding. And in each case, we see a decrease in dipole moment as well as coupling matrix elements than the actual structures where H-bonds are favourable.

**Fig. S2** Spiral and zigzag structures of octamer.



**Fig. S3** The distribution of inter-monomer angles of (a) spiral octamer, (b) zigzag octamer, (c) spiral pentamer and (d) zigzag pentamer, from AIMD trajectory.





## References -

1. Advances in Molecular Quantum Chemistry contained in the Q-Chem 4 package, Y. Shao, et al, *Molecular Physics*, **113**, 184, (2015).
2. DFTB+, a sparse matrix based implementation of the DFTB method, B. Aradi, B. Hourahine and T. Frauenheim, *Journal of Physical Chemistry A*, 111(26), 5678 (2007).