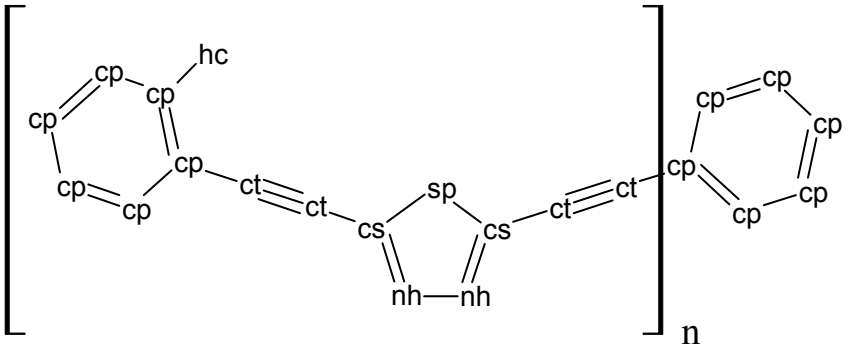
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPLEMENTARY MATERIAL

PCFF FORCE FIELD PARAMETERS DETAILS

The assignment of force field parameters starts by establishing the atom types to be used. These are summarized in the following figure:



Six atom types were used. Automatic assignment of force field parameters was used, and a careful inspection of the assignment was performed to check the possibility of missed parameters. The majority of the parameters missed were filled by using atom type equivalences which appear in the force field definition. It was particularly important to add two improper dihedrals in order to obtain a good description of the system. They are defined by atoms (cp-cp-cp)-ct and (sp-cs-nh)-ct, which have a force constant of 10 kcal/mol.

Charges were assigned from the bond increments method defined in the force field. Also, as stated in the text, in order to successfully apply the CPM to each snapshot it was necessary to modify the bond lengths and angles in the force field in order to match those from a B3LYP/6-31G* calculation. The values used were as follows:

Bond type	**r_0 (Å)**
cp-cp	1.4002
ct-cp	1.4192
ct-ct	1.2170
ct-cs	1.4053
nh-nh	1.3451
cp-hc	1.0852
cs-nh	1.3226
cs-sp	1.7600
Angle type	**α_0 (degrees)**
cp-cp-cp	120.000
hc-cp-cp	119.340
cp-cp-ct	120.490
cp-ct-ct	180.000
ct-ct-cs	180.000
nh-cs-ct	124.433
ct-cs-sp	122.288
nh-cs-sp	113.279
nh-nh-cs	113.622
cs-sp-cs	86.198

Table 1S. Calculated eigenvalues and band gap (in eV). The table presents the eigenvalues calculated for the whole 5 decamers system and for each of the decamers after deleting the remaining chains. The absolute energy levels in the isolated chains and the whole system are very different because the average potential in the supercell has been set to zero in each case, thus the vacuum levels are not aligned between the single chain systems and the whole system.

	Chain 1	Chain 2	Chain 3	Chain 4	Chain 5	Whole system
LUMO+7				-0.899		7.580
LUMO+6	-0.889	-0.929		-0.922		7.556
LUMO+5	-1.037	-0.996	-0.963	-0.997		7.442
LUMO+4	-1.106	-1.028	-1.032	-1.090	-0.902	7.417
LUMO+3	-1.161	-1.138	-1.082	-1.184	-1.098	7.397
LUMO+2	-1.297	-1.174	-1.224	-1.194	-1.173	7.344
LUMO+1	-1.418	-1.237	-1.268	-1.263	-1.225	7.329
LUMO	**-1.473**	**-1.380**	**-1.365**	**-1.315**	**-1.320**	**7.251**
HOMO	**-3.078**	**-3.087**	**-3.097**	**-3.164**	**-2.943**	**6.627**
HOMO-1	-3.229	-3.124	-3.182	-3.224	-3.014	6.509
HOMO-2	-3.284	-3.228	-3.246	-3.357	-3.159	6.435
HOMO-3	-3.355	-3.337	-3.262	-3.447	-3.270	6.394
HOMO-4	-3.434	-3.353	-3.351	-3.470	-3.329	6.325
HOMO-5	-3.524	-3.448	-3.451	-3.549	-3.380	6.306
HOMO-6	-3.550	-3.525	-3.524	-3.554	-3.396	6.291
HOMO-7	-3.567	-3.561	-3.613	-3.594	-3.516	
HOMO-8	-3.621	-3.599	-3.638	-3.624	-3.550	
HOMO-9	-3.657	-3.687	-3.657	-3.685	-3.556	
HOMO-10	-3.720	-3.720	-3.673		-3.653	
HOMO-11					-3.668	
HOMO-12					-3.691	
Band gap	1.60	1.71	1.73	1.85	1.62	0.62

Table 2S. Highest calculated absolute interchain electronic couplings (meV) for the amorphous system, conduction band. Only the highest coupling constants are shown.

		chain2	
chain1	LUMO	LUMO+1	LUMO+3
LUMO			11.1
LUMO+2		10.8	
LUMO+3	10.9		
		chain3	
	LUMO	LUMO+2	LUMO+3
LUMO	22.8		
LUMO+3		19.9	23.6
		chain4	
	LUMO+1	LUMO+3	LUMO+4
LUMO			6.6
LUMO+1			7.9
LUMO+2		21.3	
		chain5	
	LUMO+1	LUMO+3	
LUMO+1		13.1	
LUMO+2	12.4	16.4	
		chain3	
chain2	LUMO+1	LUMO+3	
LUMO+2		10.4	
LUMO+3	10.1	13.0	
		chain4	
	LUMO+1	LUMO+2	LUMO+4
LUMO		13.3	19.4
LUMO+2	12.2		
		chain5	
	LUMO+2	LUMO+3	
LUMO+1		10.2	
LUMO+4	9.5	15.8	
		chain4	
chain3	LUMO+2	LUMO+3	LUMO+4
LUMO+1		38.4	
LUMO+2	17.5		
LUMO+3			28.0
		chain5	
	LUMO	LUMO+1	LUMO+2
LUMO			8.3
LUMO+1	11.5	7.0	
		chain5	
chain4	LUMO	LUMO+1	LUMO+3
LUMO+1		7.1	
LUMO+3	9.4		
LUMO+4			6.9

Table 3S. Highest calculated absolute interchain electronic couplings (meV) for the amorphous system, valence band.

		chain2	
chain1	HOMO-2	HOMO-3	
HOMO	20.3		
HOMO-3	16.4	14.9	
		chain3	
	HOMO	HOMO-3	HOMO-4
HOMO-1	24.4		
HOMO-3		8.0	8.3
		chain4	
	HOMO-1	HOMO-2	
HOMO-1	5.6	7.4	
HOMO-3		6.3	
		chain5	
	HOMO	HOMO-1	
HOMO-2	9.9		
HOMO-3	8.0	5.0	
		chain3	
chain2	HOMO-2	HOMO-3	
HOMO-1	5.3		
HOMO-2		8.5	
HOMO-3	9.0		
		chain4	
	HOMO	HOMO-1	
HOMO-2	11.6	8.7	
HOMO-3		5.8	
		chain5	
	HOMO-1		
HOMO	18.7		
HOMO-2	9.7		
HOMO-3	7.8		
		chain4	
chain3	HOMO	HOMO-1	HOMO-2
HOMO-1	5.1	25.7	
HOMO-4			6.5
		chain5	
	HOMO-1	HOMO-2	
HOMO-1	3.2	2.8	
HOMO-3	3.2		
		chain5	
chain4	HOMO-1	HOMO-2	
HOMO-2	2.2	3.5	
HOMO-3	2.9		

Table 4S. Highest calculated absolute interchain electronic couplings (meV) between two planar cofacial PhEtTh oligomers (n=10), conduction band

3.0 Å		**chain2**	
chain1	LUMO+1	LUMO+2	LUMO+3
LUMO+1	703.6		
LUMO+2		660.3	
LUMO+3			526.9
3.5 Å	LUMO	LUMO+1	LUMO+3
LUMO	308.0		
LUMO+1		311.5	
LUMO+3			315.8
4.0 Å	LUMO+1	LUMO+2	LUMO+4
LUMO+1	152.3		
LUMO+2		142.4	
LUMO+4			142.8
4.5 Å	LUMO+2	LUMO+3	LUMO+4
LUMO+2	59.6		
LUMO+3		64.8	
LUMO+4			63.4
5.0 Å	LUMO+1	LUMO+3	LUMO+4
LUMO+1	31.1		
LUMO+3		30.9	
LUMO+4			30.6

Table 5S. Highest calculated absolute interchain electronic couplings (meV) between two planar cofacial PhEtTh oligomers (n=10), valence band

3.0 Å		**chain2**	
chain1	HOMO	HOMO-1	HOMO-3
HOMO	473.0		
HOMO-1		423.0	
HOMO-3			347.0
3.5 Å	HOMO	HOMO-2	HOMO-3
HOMO	189.1		
HOMO-2		227.6	
HOMO-3			189.1
4.0 Å	HOMO	HOMO-1	HOMO-2
HOMO	78.7		
HOMO-1		111.4	
HOMO-2			84.0
4.5 Å	HOMO	HOMO-1	HOMO-3
HOMO	32.9		
HOMO-1		30.6	
HOMO-3			35.8
5.0 Å	HOMO	HOMO-2	HOMO-3
HOMO	6.6		
HOMO-2		17.9	
HOMO-3			9.5