Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATIONS

for

A computational investigation on singlet and triplet exciton couplings in acenes molecular crystals

Claudio Quarti[a], Daniele Fazzi[b*] and Mirella Del Zoppo[a]

a. Dipartimento di Chimica, Materiali e Ing. Chimica CMIC "G. Natta", Politecnico di Milano, p.za Leonardo da Vinci 32, 20133, Milano and INSTM Udr Milano

b. Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Giovanni Pascoli, 70/3, 20133 Milano

Corresponding author: daniele.fazzi@iit.it

List of contents:

- **Singlet excited states evaluated with TD-CAM-B3LYP/6-31G** (Fig. SI14).**
- **Triplet excited states of the molecular dimers evaluated with TD-B3LYP/6-31G** (Fig. SI15)**
- **Triplet excited states evaluated with TD-CAM-B3LYP/6-31G** (Fig. SI16).**

Table SI1

Comparison between exciton couplings V for the most interacting dimers of compounds **1-4**, calculated at TD-B3LYP and TD-CAM-B3LYP/6-31G** level. Calculations have been carried out:

- in vacuo;
- in isotropic solvent ($\varepsilon = 3.5$) (IEFPCM calculations);
- anisotropic solvent ($\varepsilon_x = 4$, $\varepsilon_y = 2.5$) (IEFPCM calculations);

Compound and dimer	V_{vacuum} (cm^{-1})	IEFPCM (cm^{-1})	
		isotropic	anisotropic
Centro-symmetric dimers			
Anthracene dimer B	256	250	258
Tetracene dimer B1	134	139	133
BPEA dimer A	221	111	299 (*x* direction) (298 *z* direction)
Non-centro-symmetric dimers			
Anthracene dimer A	25	5	4
DPA dimer D	96	83	101
BPEA dimer F	215	141	272

Table SI2

Excitation energies of the first singlet and triplet excited state of BPEA evaluated at TD-DFT with PBEPBE, B3LYP, PBE0, BHandH, CAM-B3LYP exchange-correlation functionals and 6-31G**, cc-pVTZ basis sets.

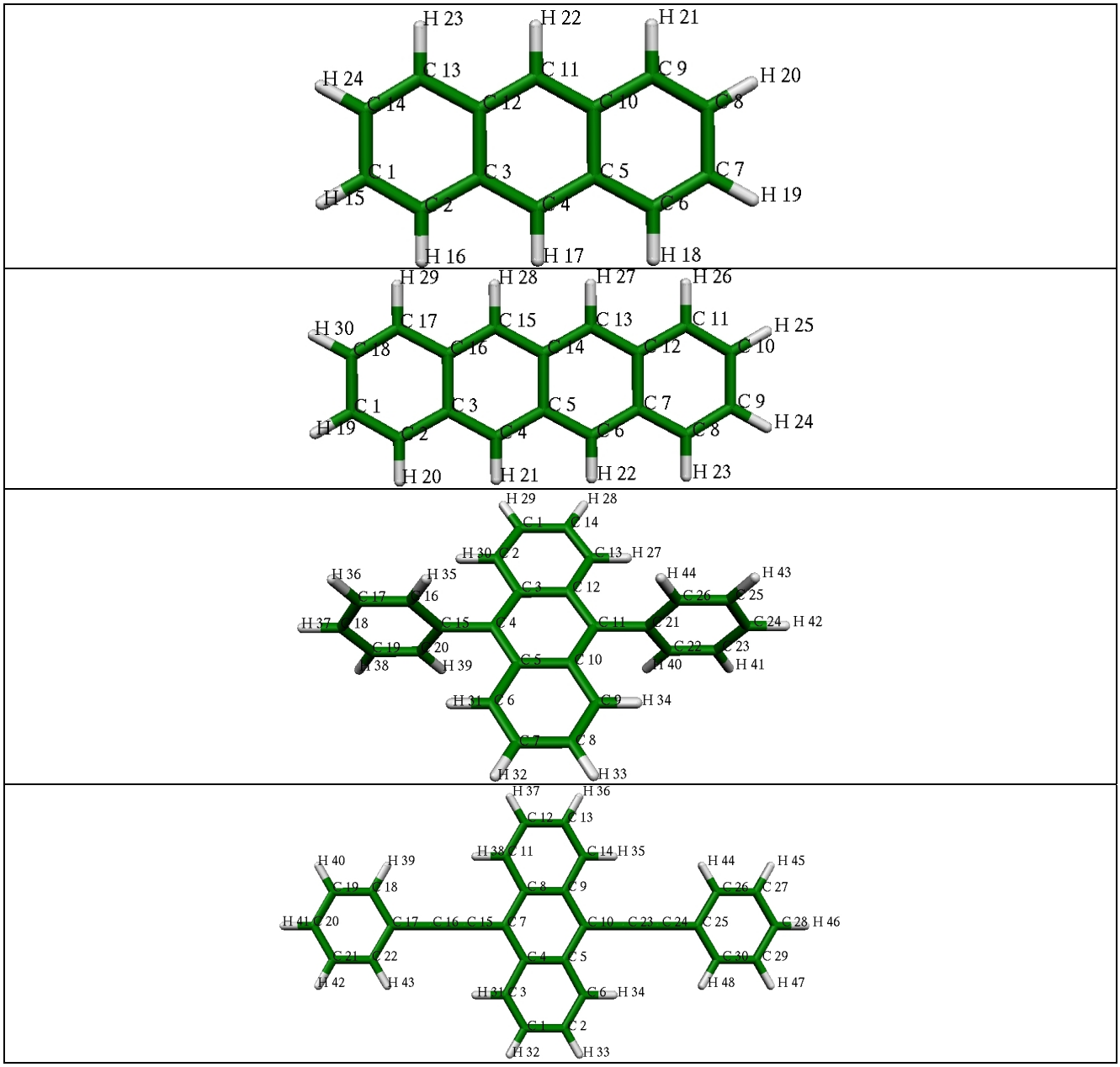
Functional	6-31G**	cc-pVTZ	experimental
T_1 state excitation energies (cm^{-1})			
PBEPBE	17410	17320	
B3LYP	19870	19570	

PBE1PBE	20510	20350	
BHANDH	23350	23070	
CAM-B3LYP	23160	-------	21780

S_1 state excitation energies ($cm^{-1)}$

PBEPBE	9998	10228	
B3LYP	10057	10165	
PBE1PBE	9206	9570	
BHANDH	8417	9227	
CAM-B3LYP	8922	-------	12480

Figure SI1: atom numbering of anthracene, tetracene, DPA and BPEA (see also Fig. 2 in the manuscript).



Unit cell

Fig SI2: ANTHRACENE

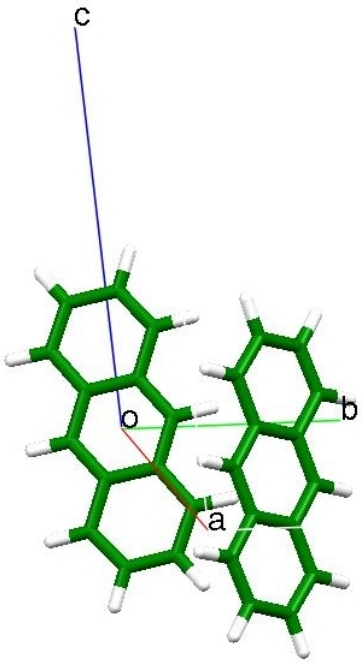


Fig. SI3: TETRACENE

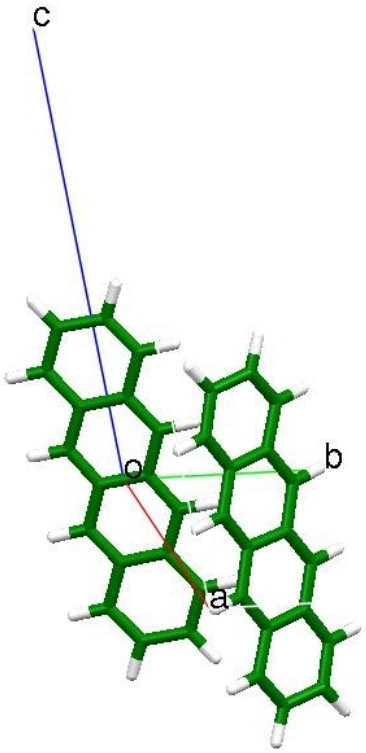


Fig. SI4: DPA

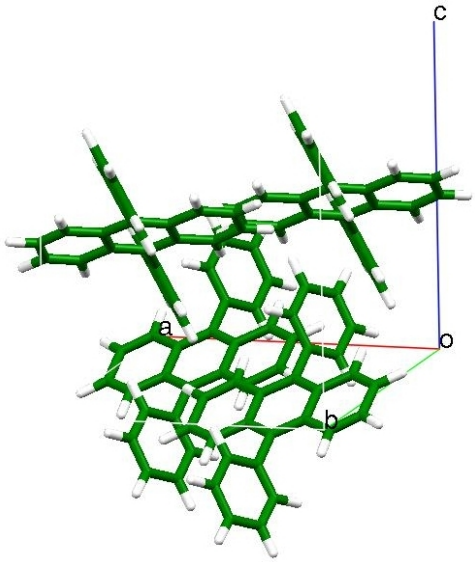
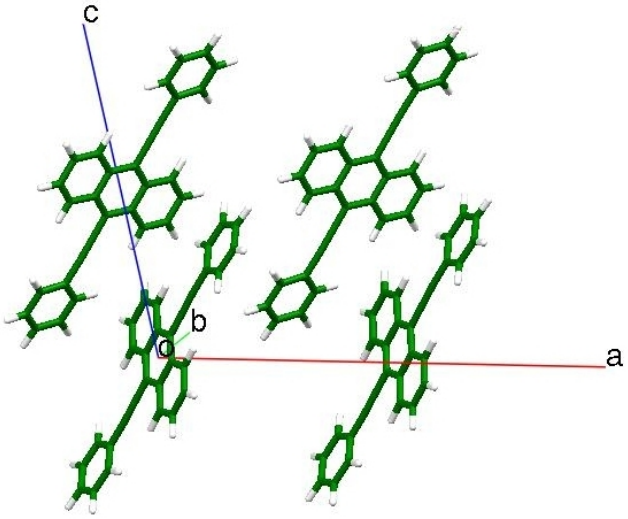


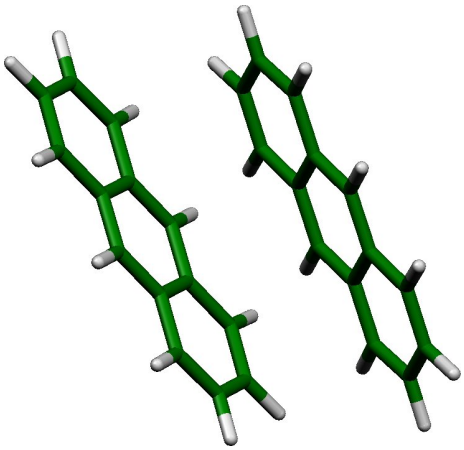
Fig SI5: BPEA



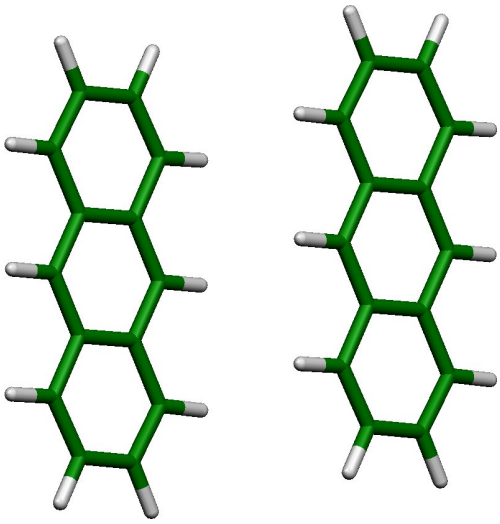
MOLECULAR DIMERS

Fig. SI6: ANTHRACENE

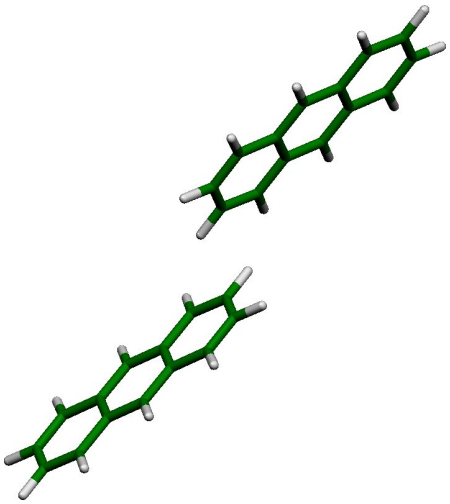
DIMER A



DIMER B



DIMER C



DIMER D

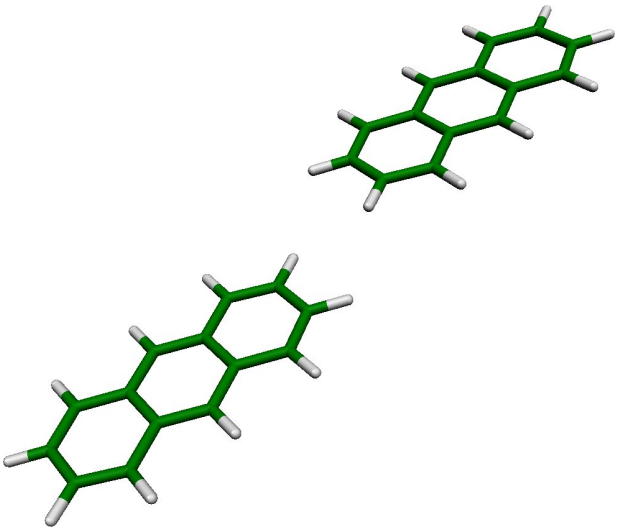
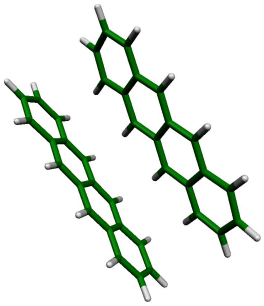
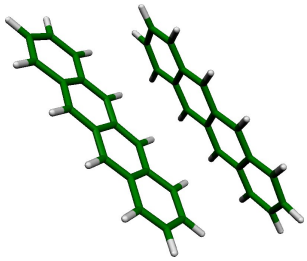


Fig. SI7: TETRACENE

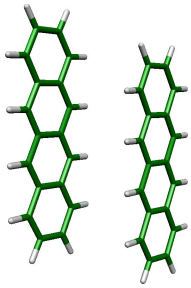
DIMER A



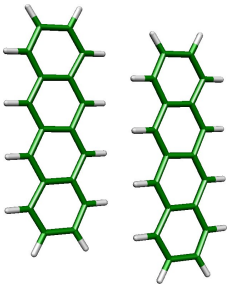
DIMER A1



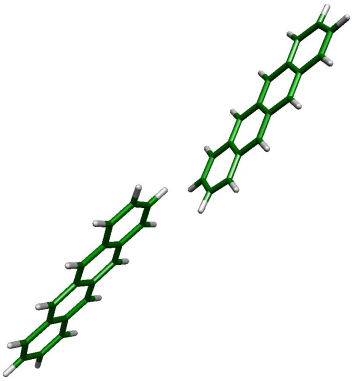
DIMER B



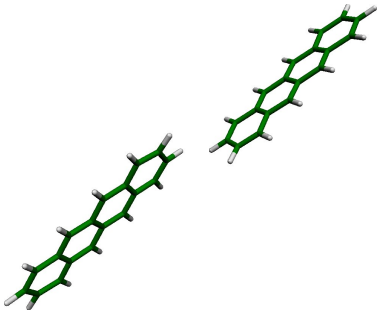
DIMER B1



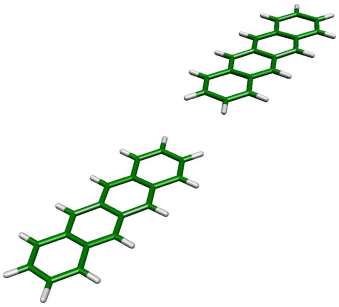
DIMER C



DIMER C1



DIMER D



DIMER D1

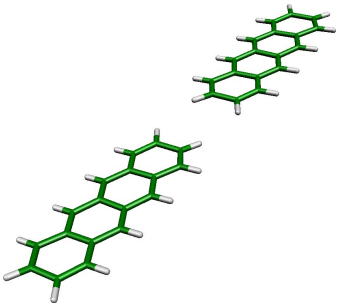
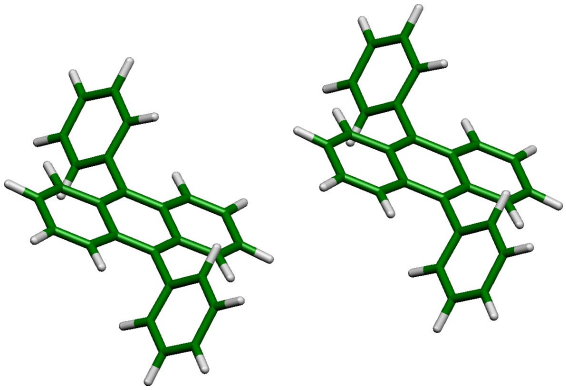
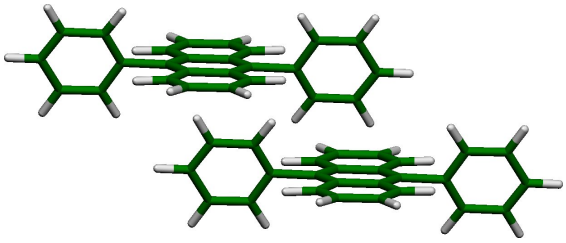


Fig. SI8: DPA

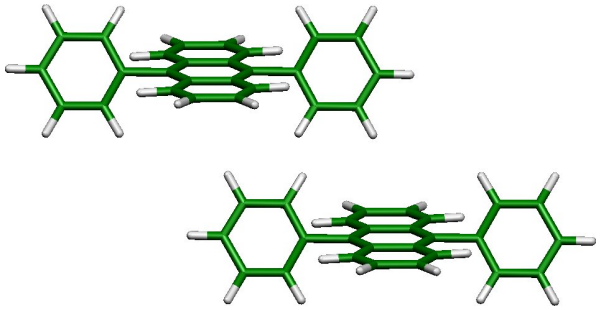
DIMER A



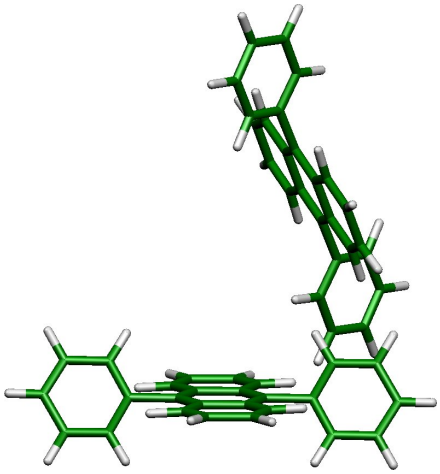
DIMER B



DIMER C



DIMER D



DIMER E

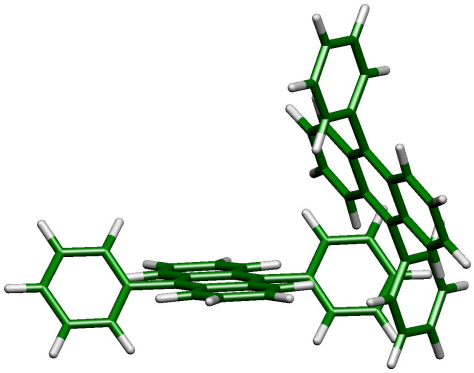
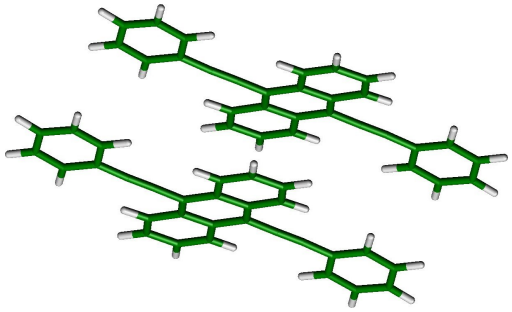
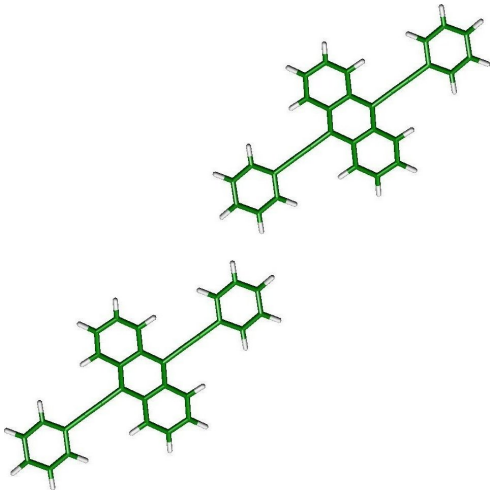


Fig. SI9: BPEA

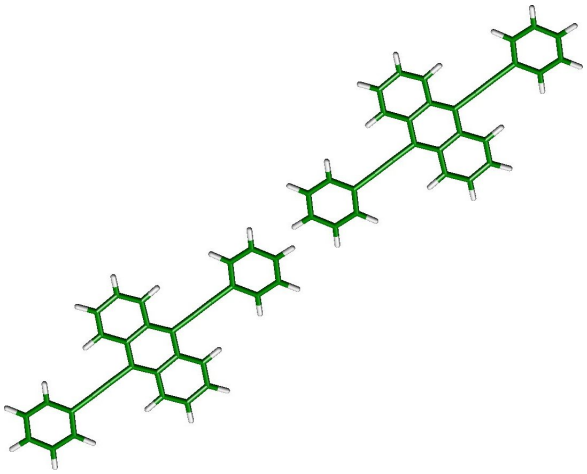
DIMER A



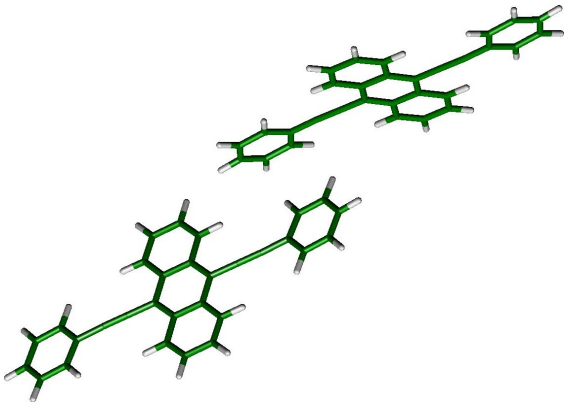
DIMER B



DIMER C



DIMER D



DIMER F

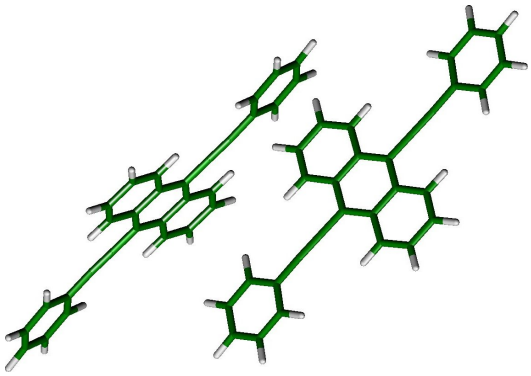


Table SI3: TD-B3LYP and TD-CAM-B3LYP/6-31G** exciton couplings V (cm^{-1}) evaluated with the Point Dipole Approximation (PDA) method. In Table we report also the TDDFT exciton couplings as evaluated within the supramolecular approach.

TD-B3LYP

PDA

ANTHRACENE		tetracene		DPA		BPEA	
A	41	A	424	A	282	A	**16849**
B	**1088**	A1	**1226**	B	**740**	B	740
C	198	B	629	C	36	C	799
D	119	B1	464	D	91	D	1973
		C	113	E	444	F	2399
		C1	33				
		D	63				
		D1	23				

supramolecular approach

ANTHRACENE		tetracene		DPA		BPEA	
A	121	A	---	A	29	A	**754**
B	**157**	A1	**369**	B	**313**	B	165
C	12	B	8	C	48	C	291
D	15	B1	107	D	80	D	255
		C	247	E	265	F	212
		C1	232				
		D	113				
		D1	80				

TD-CAM-B3LYP

PDA

ANTHRACENE		tetracene		DPA		BPEA	
A	54	A	576	A	299	A	**16572**
B	**1470**	A1	**1686**	B	**624**	B	734
C	268	B	797	C	114	C	793
D	161	B1	646	D	97	D	1971
		C	152	E	446	F	2314
		C1	47				
		D	78				
		D1	33				

supramolecular approach

ANTHRACENE		tetracene		DPA		BPEA	
A	29	A	---	A	23	A	**221**
B	**256**	A1	---	B	50	B	**160**
C	27	B	13	C	61	C	**231**
D	21	B1	**134**	D	**96**	D	**262**
		C	83	E	25	F	**215**
		C1	---				
		D	25				
		D1	2				

TRANSITION DENSITY MATRIX (TDM) PROJECTIONS

The coefficients of the projection of the transition density matrices, evaluated at ZINDO/S level, are reported (for further details on the method see also ref 48 in the manuscript).

Table SI4: ANTHRACENE

	(a,ab)				(b,ab)			
	S1	S2	S3	S4	S1	S2	S3	S4
Dimer A								
S1	-0.65	0.00	0.00	-0.03	0.76	0.01	0.00	0.00
S2	-0.76	-0.01	0.00	0.03	-0.64	0.01	0.01	0.01
Dimer B								
S1	-0.71	-0.01	0.00	0.00	-0.70	-0.01	0.00	0.00
S2	-0.71	0.01	0.00	0.01	0.71	-0.01	0.00	0.01
Dimer C								
S1	0.79	0.00	0.00	0.00	-0.61	0.01	0.00	0.02
S2	0.61	0.00	-0.01	-0.01	0.79	0.02	0.00	0.01
Dimer D								
S1	-0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S2	-0.71	0.00	0.00	0.00	-0.71	0.00	0.00	0.00

Table SI5: TETRACENE

	(a,ab)				(b,ab)			
	S1	S2	S3	S4	S1	S2	S3	S4
Dimer A								
S1	-0.14	0.01	0.01	0.00	-0.99	0.00	0.00	0.00
S2	-0.98	-0.01	0.00	0.00	0.13	0.02	0.02	-0.01
Dimer A1								
S1	-0.25	0.00	0.00	0.00	-0.96	0.00	0.00	0.00
S2	-0.96	0.00	0.00	0.01	0.25	0.00	0.00	0.00
Dimer B								
S1	-0.70	-0.01	-0.02	0.00	0.70	0.01	-0.02	0.00
S2	0.70	-0.01	-0.02	-0.01	0.70	-0.01	0.02	0.01
Dimer B1								
S1	-0.71	-0.01	0.01	0.00	-0.71	-0.01	-0.01	0.00
S2	0.71	-0.01	0.01	0.00	-0.71	0.01	0.01	0.00
Dimer C								
S1	0.05	0.00	0.00	0.00	-1.00	0.00	0.00	0.00
S2	1.00	0.00	0.00	0.00	0.05	0.02	0.00	0.00
Dimer C1								
S1	0.05	0.00	0.00	0.00	-1.00	0.00	0.00	0.00
S2	1.00	0.00	0.00	0.00	0.02	-0.01	0.00	0.00
Dimer D								
S1	0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S2	0.71	0.00	0.00	0.00	-0.71	0.00	0.00	0.00
Dimer D1								
S1	0.70	0.00	0.00	0.00	0.72	0.00	0.00	0.00
S2	0.72	0.00	0.00	0.00	-0.70	0.00	0.00	0.00

TABLE SI6: DPA

NOTE: the low lying dipole allowed excited states of the isolated DPA molecule, based on the experimental X-ray structure, is the S2 state.

	(a,ab)				(b,ab)			
	S1	S2	S3	S4	S1	S2	S3	S4
Dimer A								
S1	0.71	0.00	0.00	-0.01	0.71	0.00	0.00	-0.01
S2	-0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S3	0.00	0.71	0.00	0.00	0.00	-0.71	0.00	0.00
S4	0.00	-0.71	0.00	0.01	0.00	-0.71	0.00	0.01
Dimer B								
S1	0.70	0.04	0.00	0.00	-0.71	-0.04	0.00	0.00
S2	0.71	-0.03	0.00	0.00	0.71	-0.03	0.00	0.00
S3	0.04	-0.70	0.00	-0.01	-0.04	0.71	0.00	0.01
S4	0.03	0.71	0.00	-0.02	0.03	0.70	0.00	-0.02
Dimer C								
S1	-0.71	-0.03	0.00	0.00	-0.71	-0.03	0.00	0.00
S2	-0.71	0.03	0.00	0.00	0.71	-0.03	0.00	0.00
S3	0.03	-0.71	0.00	-0.01	0.03	-0.71	0.00	-0.01
S4	0.03	0.71	0.00	-0.01	-0.03	-0.71	0.00	0.01
Dimer D								
S1	-0.54	-0.03	0.00	0.00	-0.84	-0.03	0.00	0.00
S2	-0.84	0.02	0.00	0.00	0.54	-0.03	0.00	0.01
S3	0.03	-0.70	0.00	0.00	0.03	-0.71	0.00	0.00
S4	-0.02	-0.71	0.00	0.00	0.02	0.70	0.00	0.00
Dimer E								
S1	-0.75	0.01	0.00	0.00	-0.66	0.01	0.00	0.00
S2	-0.66	-0.01	0.00	0.00	0.75	0.01	0.00	0.00
S3	-0.01	-0.71	0.00	0.01	-0.01	-0.70	0.00	-0.01
S4	0.01	-0.70	0.00	-0.01	-0.01	0.71	0.00	-0.01

Table SI7: BPEA

	(a,ab)				(b,ab)			
	S1	S2	S3	S4	S1	S2	S3	S4
Dimer A								
S1	-0.70	0.00	0.00	0.00	0.70	0.00	0.00	0.00
S2	0.68	-0.01	0.00	0.00	0.68	-0.01	0.00	0.00
Dimer B								
S1	0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S2	-0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
Dimer C								
S1	0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S2	0.71	0.00	0.00	0.00	-0.71	0.00	0.00	0.00
Dimer D								
S1	-0.72	0.00	0.00	0.00	-0.69	0.00	0.00	0.00
S2	0.69	0.00	0.00	0.00	-0.72	0.00	0.00	0.00
Dimer F								
S1	-0.71	0.00	0.00	0.00	0.71	0.00	0.00	0.00
S2	-0.71	0.01	0.00	0.00	-0.71	0.01	0.00	0.00

Properties of the singlet excited states of the dimers evaluated at B3LYP/6-31G level:** excitation energies, oscillator strength, molecular orbitals involved and TD-DFT eigenvectors are reported.

Table SI8: ANTHRACENE

State	energy (eV)	f	orbitals		MO coefficients
Dimer A					
S1	2.7091	0.0041	H	L	0.70
S2	3.2087	0.0465	H-1	L	0.63
			H-1	L+1	0.14
S3	3.2387	0.0626	H	L	0.64
S4	3.4194	0.0084	H-1	L+1	0.69
Dimer B					
S1	3.0756	0.0548	H-1	L+1	0.23
			H	L	0.65
S2	3.1146	0.0000	H-1	L	0.50
			H	L+1	0.50
S3	3.2623	0.0000	H-1	L	0.45
			H	L+1	-0.44
S4	3.2641	0.1029	H-1	L+1	0.63
			H	L	-0.17
Dimer C					
S1	3.1669	0.0026	H	L	0.70
S2	3.2433	0.0342	H-1	L	0.60
			H	L+1	-0.22
S3	3.2463	0.0834	H-1	L	0.22
			H	L+1	0.60
S4	3.3171	0.0031	H-1	L+1	0.70
Dimer D					
S1	3.2404	0.0000	H-1	L	0.47
			H	L+1	0.43
S2	3.2443	0.1166	H-1	L+1	0.43
			H	L	0.47
S3	3.2728	0.0000	H-1	L	-0.48
			H	L+1	0.52
S4	3.2729	0.0003	H-1	L+1	0.52
			H	L	-0.48

Table SI9: TETRACENE

state	energy (eV)	f	orbitals		MO coefficients
Dimer A					
S1	1.8146	0.0056	H	L	0.70
S2	2.3760	0.0600	H-1	L+1	-0.11
S3	2.4362	0.0443	H-1	L	0.61
			H-1	L+1	-0.17
S4	2.6299	0.0210	H-1	L	0.14
			H-1	L+1	0.67
Dimer A1					
S1	1.8374	0.0060	H	L	0.7
S2	2.3484	0.0343	H-1	L	0.61
			H-1	L+1	0.13
S3	2.4737	0.0737	H	L+1	0.62
S4	2.5979	0.0082	H-1	L+1	0.69
Dimer B					
S1	2.2996	0.0000	H-1	L	0.58
			H	L+1	0.4
S2	2.3000	0.0144	H-1	L+1	0.39
			H	L	0.58
S3	2.4774	0.0000	H-1	L	-0.33
			H	L+1	0.54
S4	2.4794	0.1549	H-1	L+1	0.54
Dimer B1			H	L	-0.32
S1	2.2106	0.0000	L-1	H+1	-0.44
			H	L	0.55
S2	2.2134	0.0007	H-1	L	0.52
			H	L+1	-0.48
S3	2.3746	0.1215	H-1	L	0.42
			H	L+1	0.46
S4	2.4011	0.0000	H-1	L+1	0.5
			H	L	0.37
Dimer C					
S1	2.3863	0.0183	H-1	L	-0.12
			H	L	0.67
S2	2.3957	0.0414	H-1	L	0.64
S3	2.4788	0.0906	H-1	L+1	-0.17
			H	L+1	0.61
S4	2.4918	0.0160	H-1	L	0.65

			H	L+1	0.24
Dimer C1					
S1	2.3922	0.0512	H	L	0.6
			H	L+1	0.19
S2	2.4163	0.0037	H	L	-0.26
			H	L+1	0.65
S3	2.4710	0.0904	H-1	L	0.52
			H-1	L+1	-0.36
S4	2.4954	0.0068	H-1	L	0.44
			H-1	L+1	0.55
Dimer D					
S1	2.4736	0.1956	H-1	L	0.5
			H	L+1	-0.37
S2	2.4775	0.0000	H-1	L+1	-0.31
			H	L	0.55
S3	2.5008	0.0032	H-1	L	0.44
			H	L+1	0.55
S4	2.5017	0.0000	H-1	L+1	0.59
			H	L	0.38
Dimer D1					
S1	2.3895	0.0018	H-1	L+1	0.4
			H	L	0.46
S2	2.3898	0.1107	H-1	L	0.43
			H	L+1	0.44
S3	2.4092	0.0000	H-1	L	0.5
			H	L+1	-0.5
S4	2.4092	0.0000	H-1	L+1	0.52
			H	L	-0.47

Table SI10: DPA

state	energy (eV)	f	orbitals		MO coefficients
Dimer A					
S1	3.5913	0.0000	H-1	L+1	-0.33
			H	L	0.56
S2	3.5984	0.2777	H-1	L	0.55
			H	L+1	-0.34
S3	3.7193	0.0128	H-1	L	0.39
			H	L+1	0.58

S4	3.7207	0.0000	H-1	L+1	0.59
			H	L	0.38
Dimer B					
S1	3.5965	0.0000	H-1	L	-0.25
			H	L+1	0.60
S2	3.6743	0.0000	H-1	L	0.63
			H	L+1	0.31
S3	3.6743	0.0000	H-1	L	0.63
			H	L+1	0.31
S4	3.6859	0.0533	H-1	L+1	0.65
			H	L	0.24
Dimer C					
S1	3.5921	0.0000	H-1	L+1	0.41
			H	L	0.50
S2	3.6041	0.2800	H-1	L	0.46
			H	L+1	0.45
S3	3.6806	0.0002	H-1	L	-0.50
			H	L+1	0.50
S4	3.6811	0.0000	H-1	L+1	0.54
			H	L	-0.46
Dimer D					
S1	3.5967	0.1121	H-1	L+1	0.45
			H	L	0.47
S2	3.6166	0.1938	H-1	L	0.46
			H	L+1	0.45
S3	3.6754	0.0000	H-1	L	-0.5
			H	L+1	0.5
S4	3.6754	0.0001	H-1	L+1	0.51
			H	L	-0.49
Dimer E					
S1	3.5916	0.0829	H-1	L	0.26
			H	L+1	0.6
S2	3.5951	0.1533	H-1	L+1	0.19
			H	L	0.63
S3	3.6521	0.0079	H-1	L	0.62
			H	L+1	-0.31
S4	3.6573	0.0363	H-1	L+1	0.65
			H	L	-0.25

Table SI11: BPEA

state	energy (eV)	f	orbitals		MO coefficients
Dimer A					
S1	2.2033	0.1778	H-1	L+1	-0.29
			H	L	0.63
S2	2.2421	0.0000	H-1	L	0.61
			H	L+1	-0.34
S3	2.4720	0.0000	H-1	L	0.28
			H	L+1	0.57
S4	2.6589	1.1059	H-1	L+1	0.60
Dimer B			H	L	0.21
S1	2.5270	1.7293	H-1	L	0.44
			H	L+1	0.44
S2	2.5628	0.0000	H-1	L+1	-0.47
			H	L	0.53
S3	2.5629	0.0000	H-1	L	-0.50
			H	L+1	0.50
S4	2.5678	0.0000	H-1	L+1	0.47
			H	L	0.40
Dimer C					
S1	2.5020	1.5596	H-1	L+1	-0.19
			H	L	0.61
S2	2.5594	0.0000	H-1	L	0.55
			H	L+1	0.44
S3	2.5732	0.2613	H-1	L+1	0.64
			H	L	0.26
S4	2.5741	0.0000	H-1	L	-0.37
			H	L+1	0.50
Dimer D					
S1	2.3565	0.0029	H	L	0.71
S2	2.5103	1.6951	H-1	L	0.45
			H	L+1	0.43
S3	2.5736	0.0262	H-1	L	-0.43
			H	L+1	0.45
S4	2.6121	0.0035	H-1	L+1	0.71
Dimer F					
S1	2.3737	0.0002	H-1	L+1	-0.46
			H	L	0.53
S2	2.3744	0.0011	H-1	L	0.51

			H	L+1	-0.49
S3	2.5099	0.0384	H-1	L+1	0.48
			H	L	0.40
S4	2.5626	1.4381	H-1	L	0.43
			H	H+1	0.45

High density planes for anthracene, tetracene and BPEA molecular crystals

Fig. SI10: ANTHRACENE

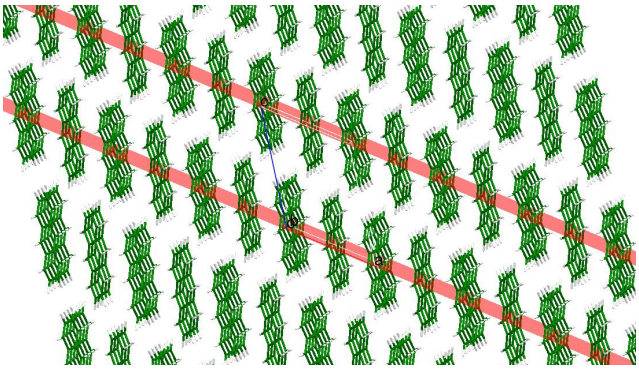


Fig. SI11: TETRACENE

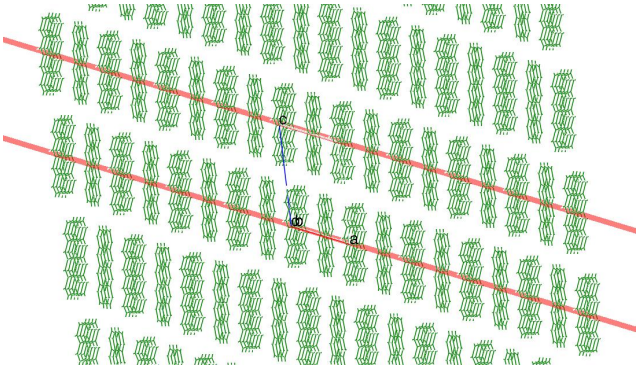


Fig. SI12: BPEA

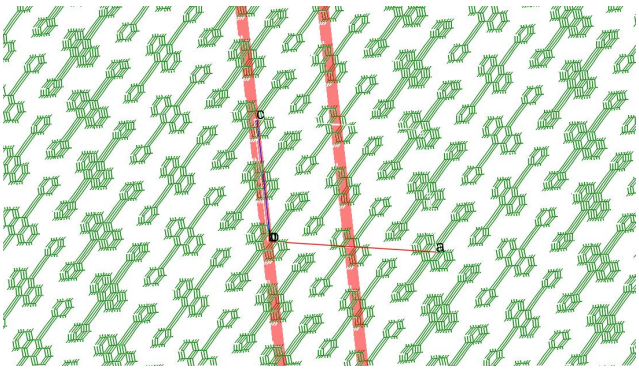
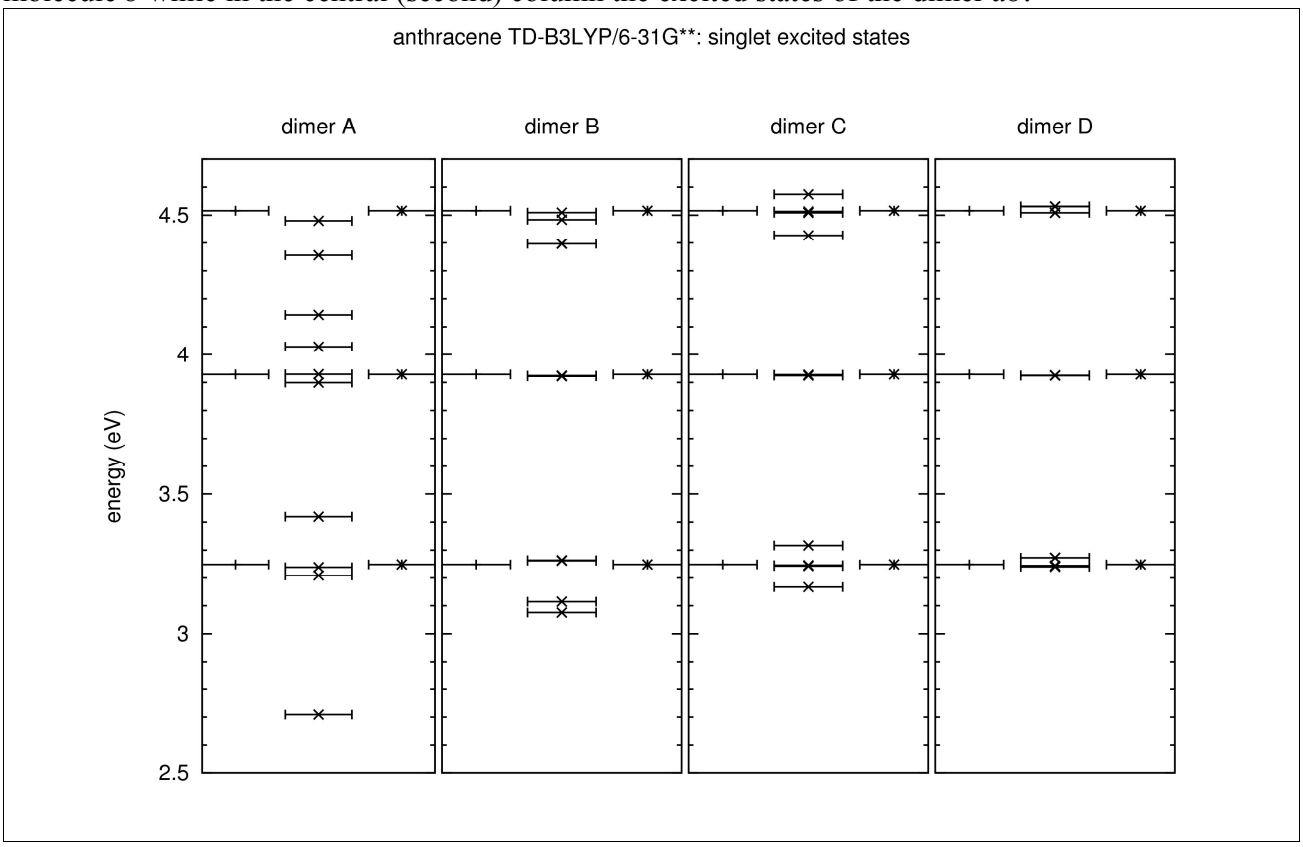
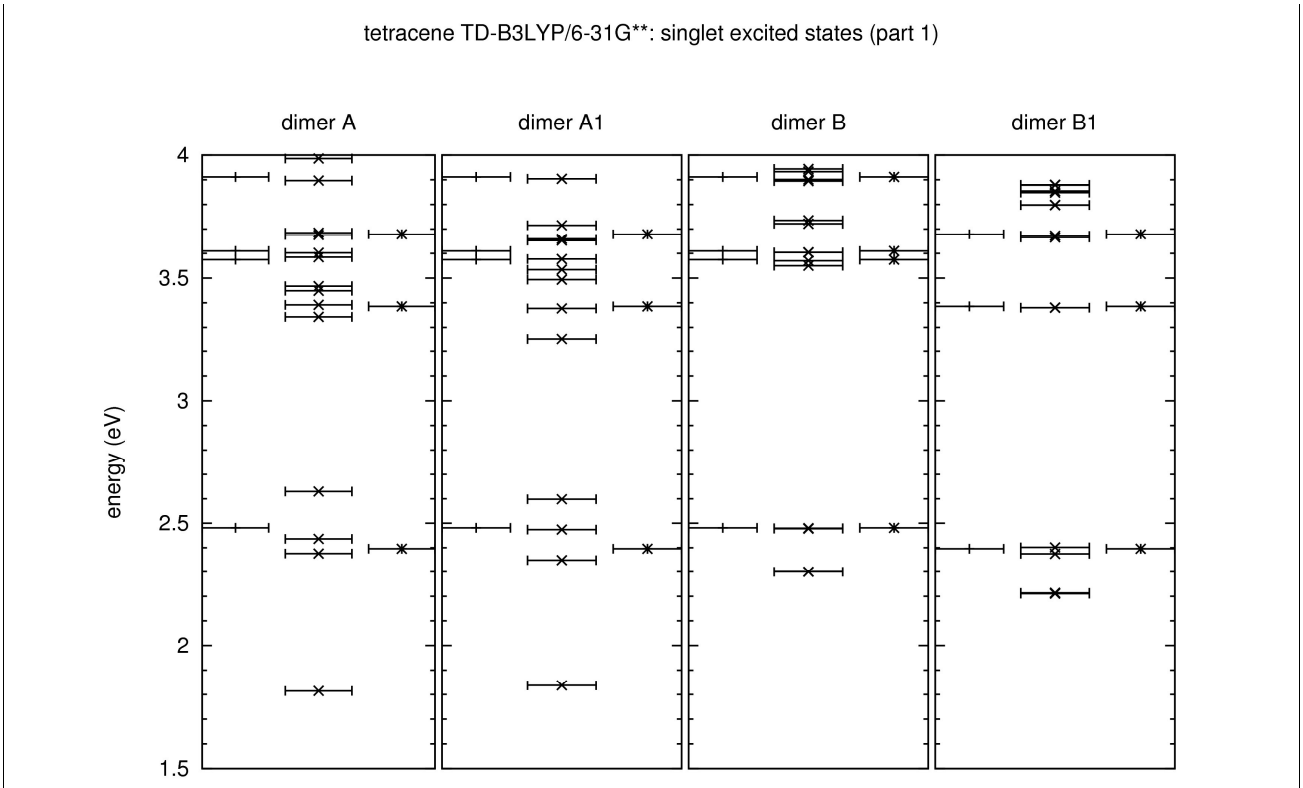
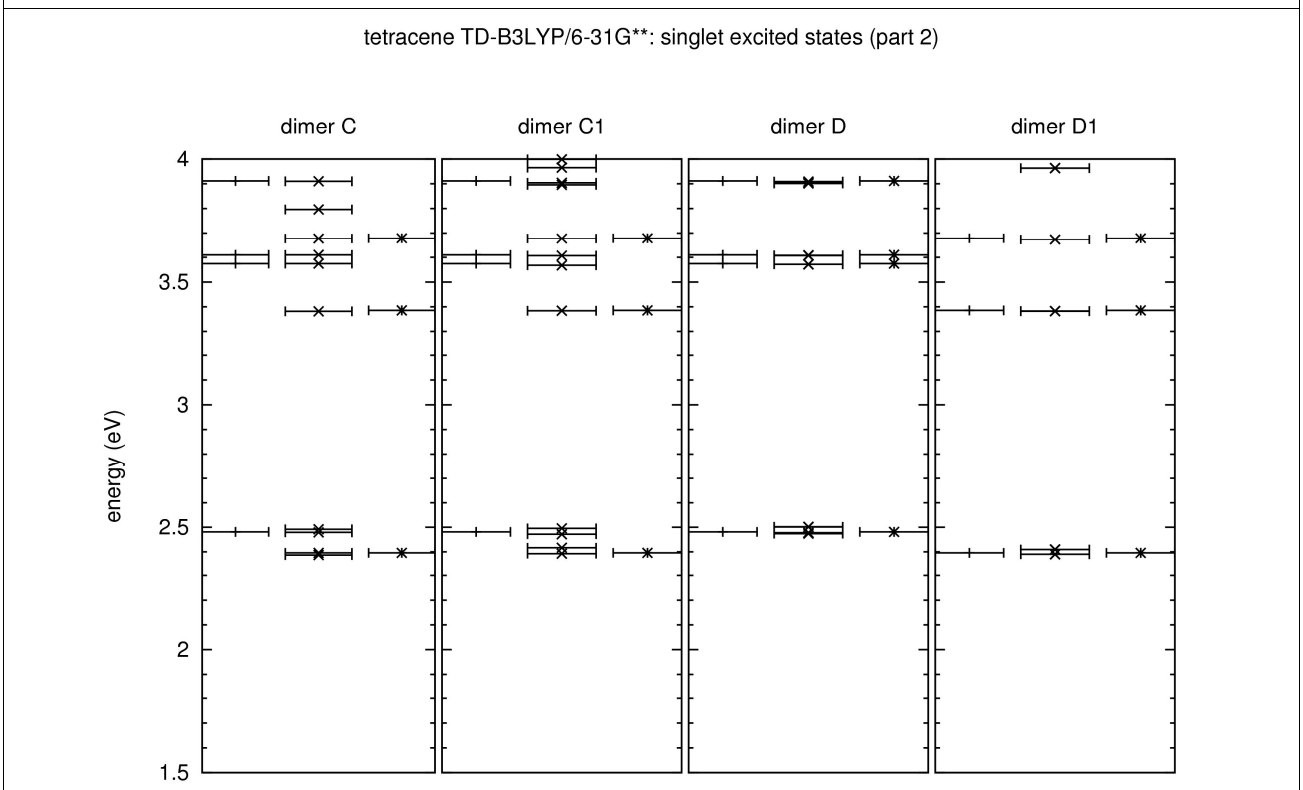


Fig. SI13: TD-B3LYP/6-31G SINGLET EXCITED STATES OF THE DIMERS**

In the panels below reported (SI13-SI16) for each dimer and for each molecular crystal, we considered in the first column the excited state energies of molecule *a*, in the third column the excited states of molecule *b* while in the central (second) column the excited states of the dimer *ab*.







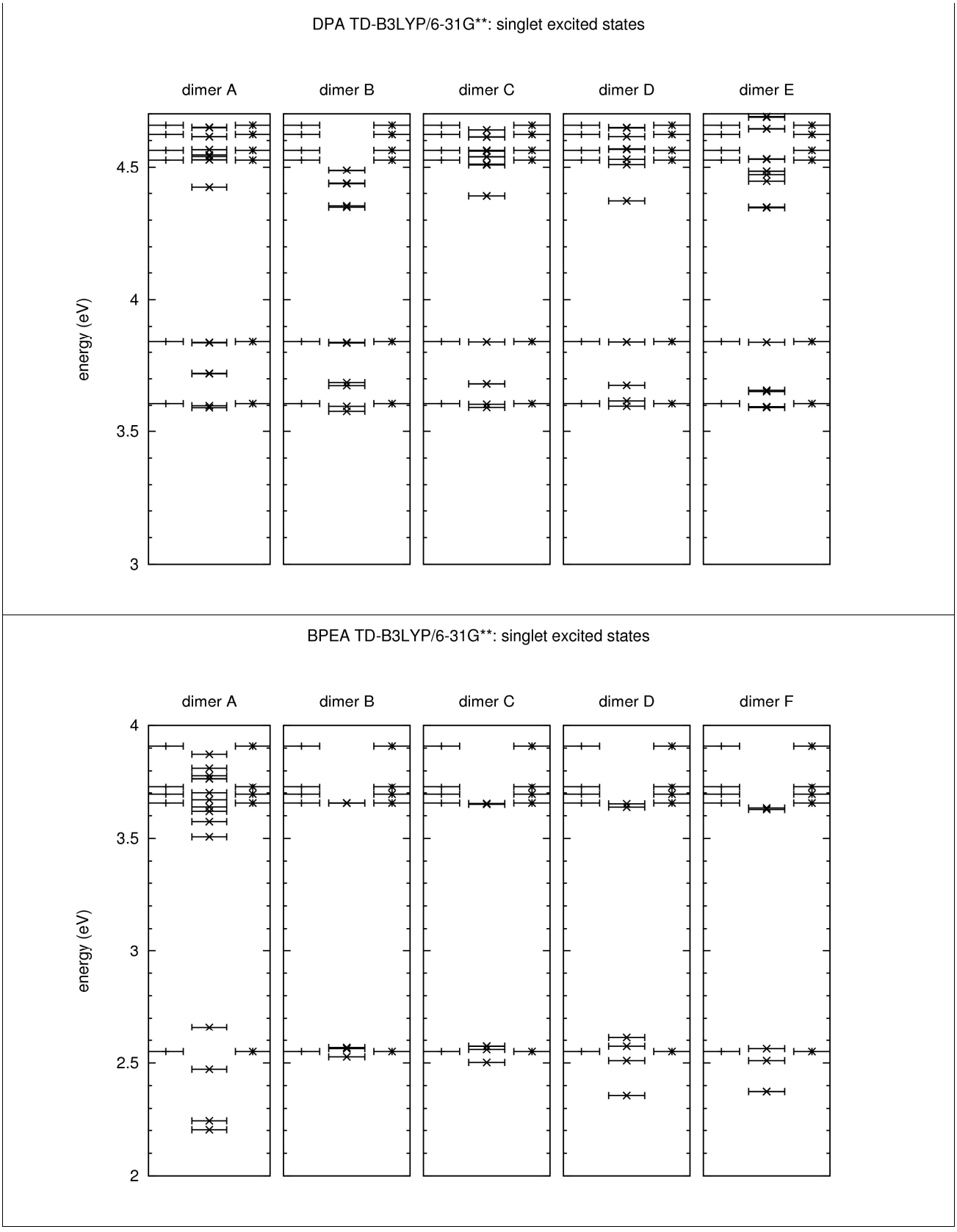
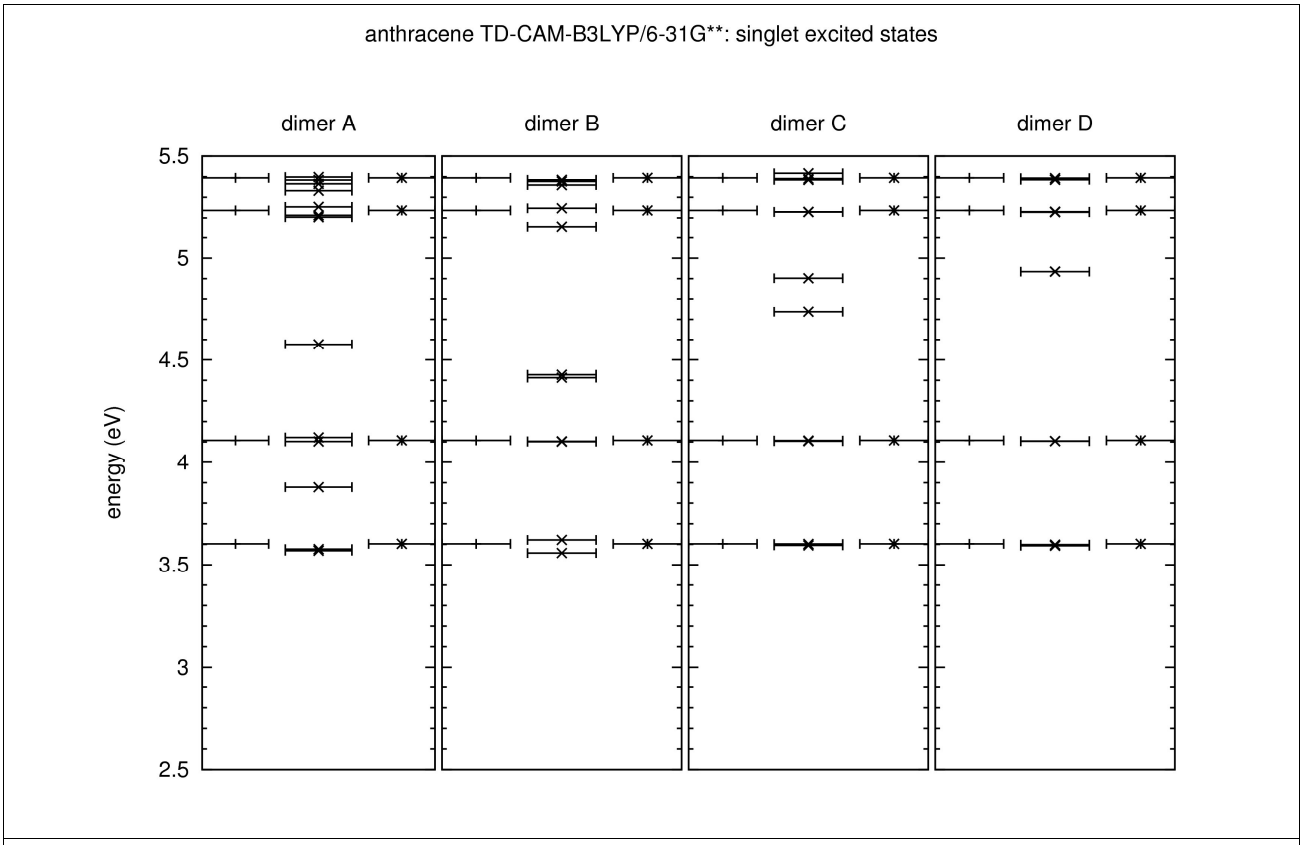
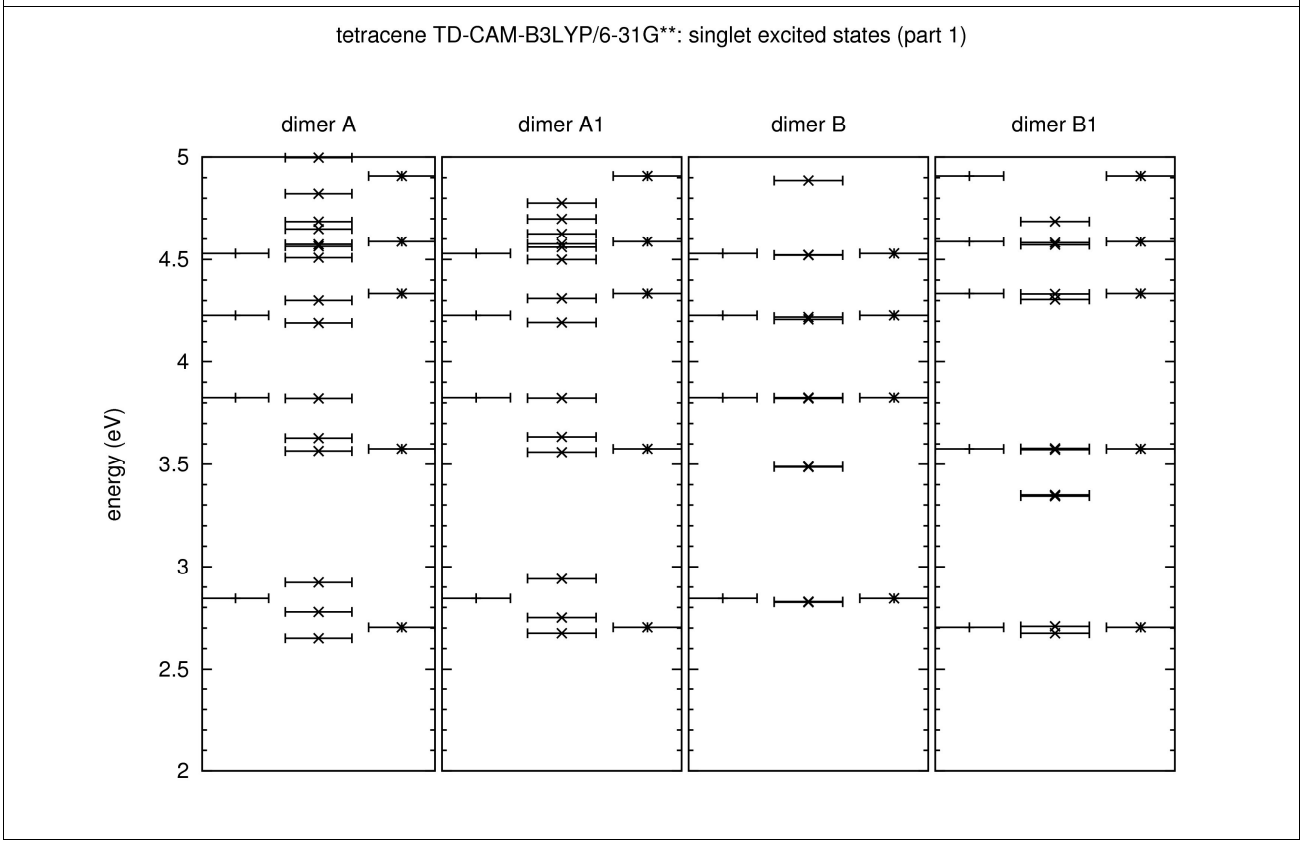
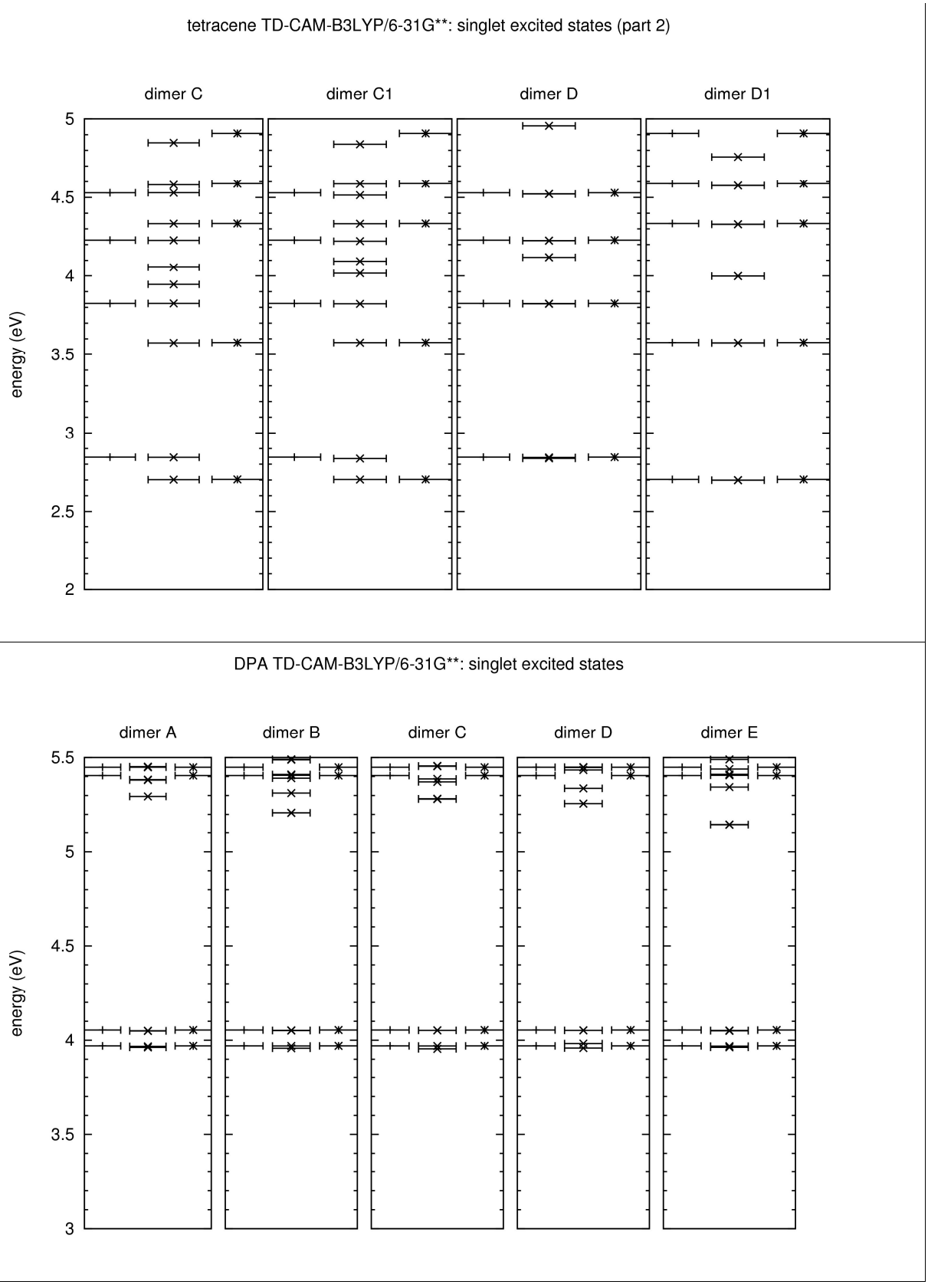


Fig. SI14: TD-CAM-B3LYP/6-31G SINGLET EXCITED STATES**







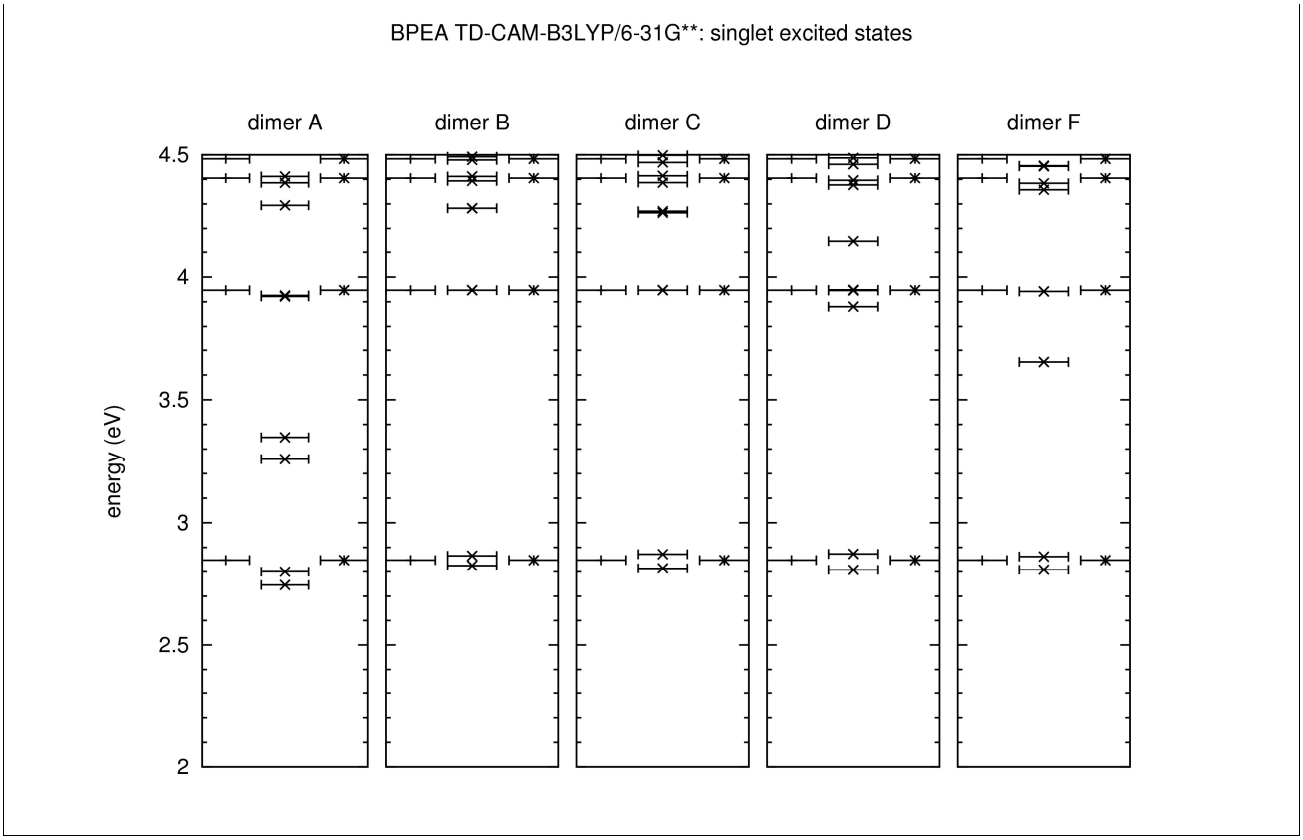
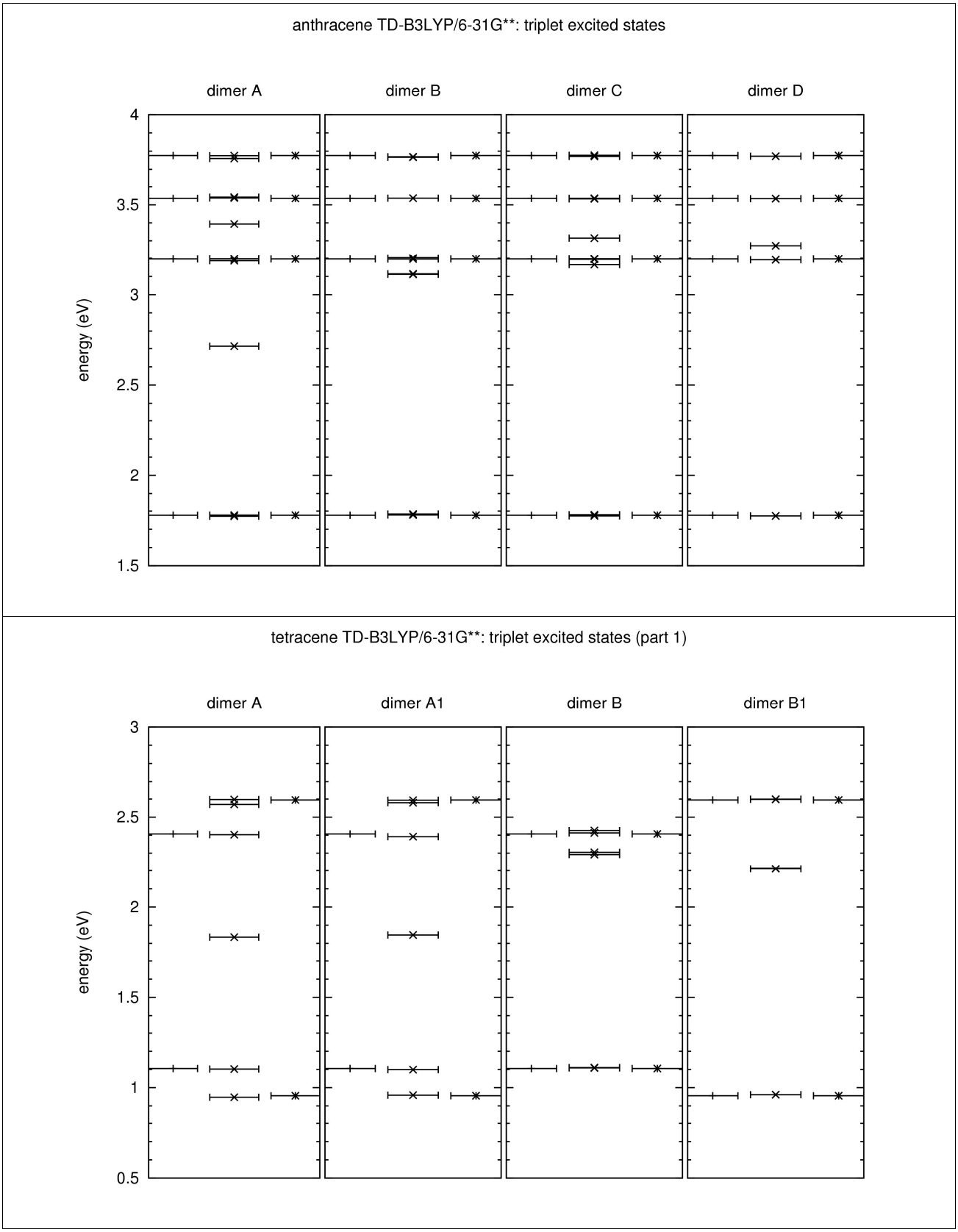
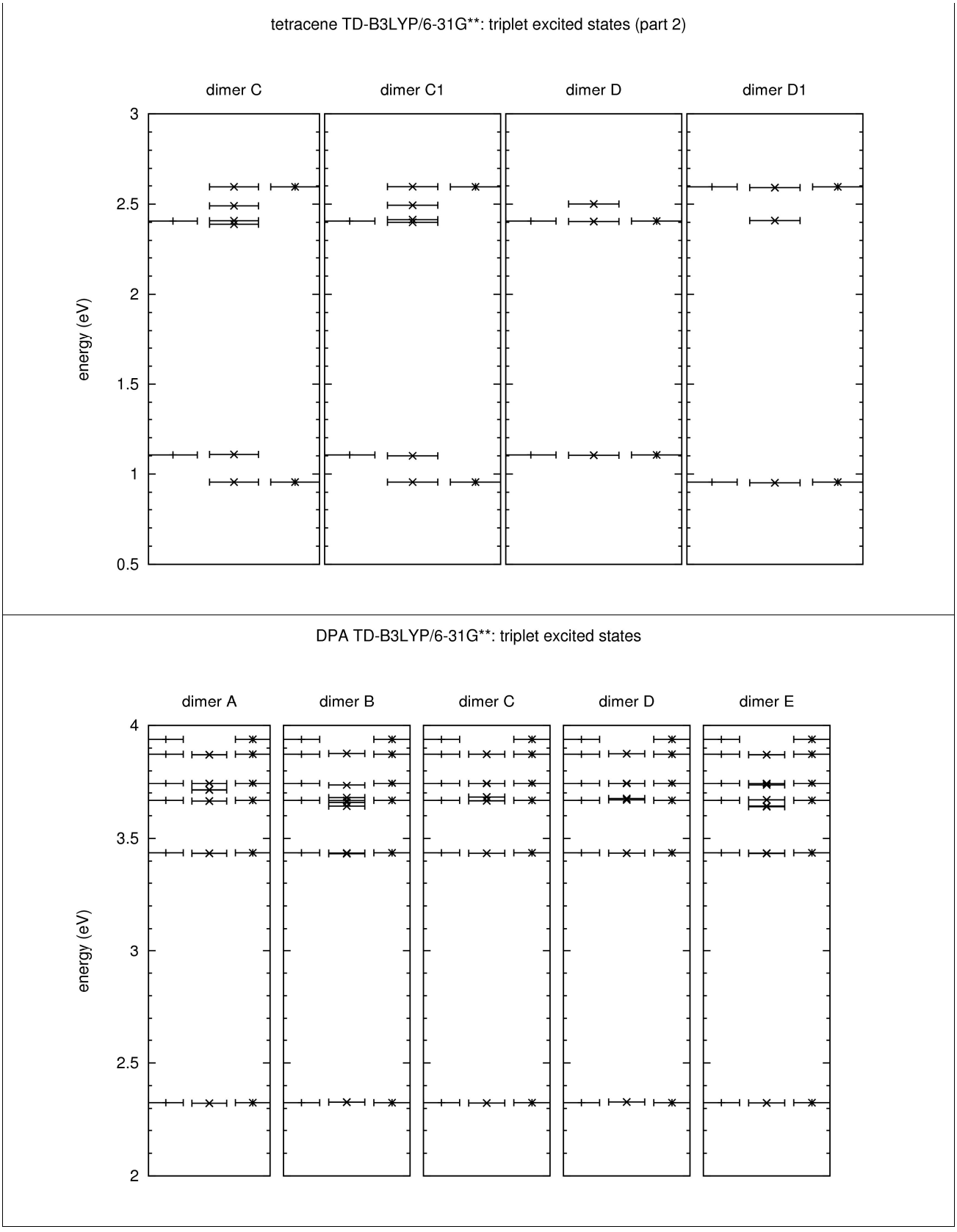

BPEA TD-CAM-B3LYP/6-31G**: singlet excited states
dimer A
dimer B
dimer C
dimer D
dimer F
energy (eV)
4.5
4
3.5
3
2.5
2

Fig. SI15: TD-B3LYP/6-31G TRIPLET EXCITED STATES**





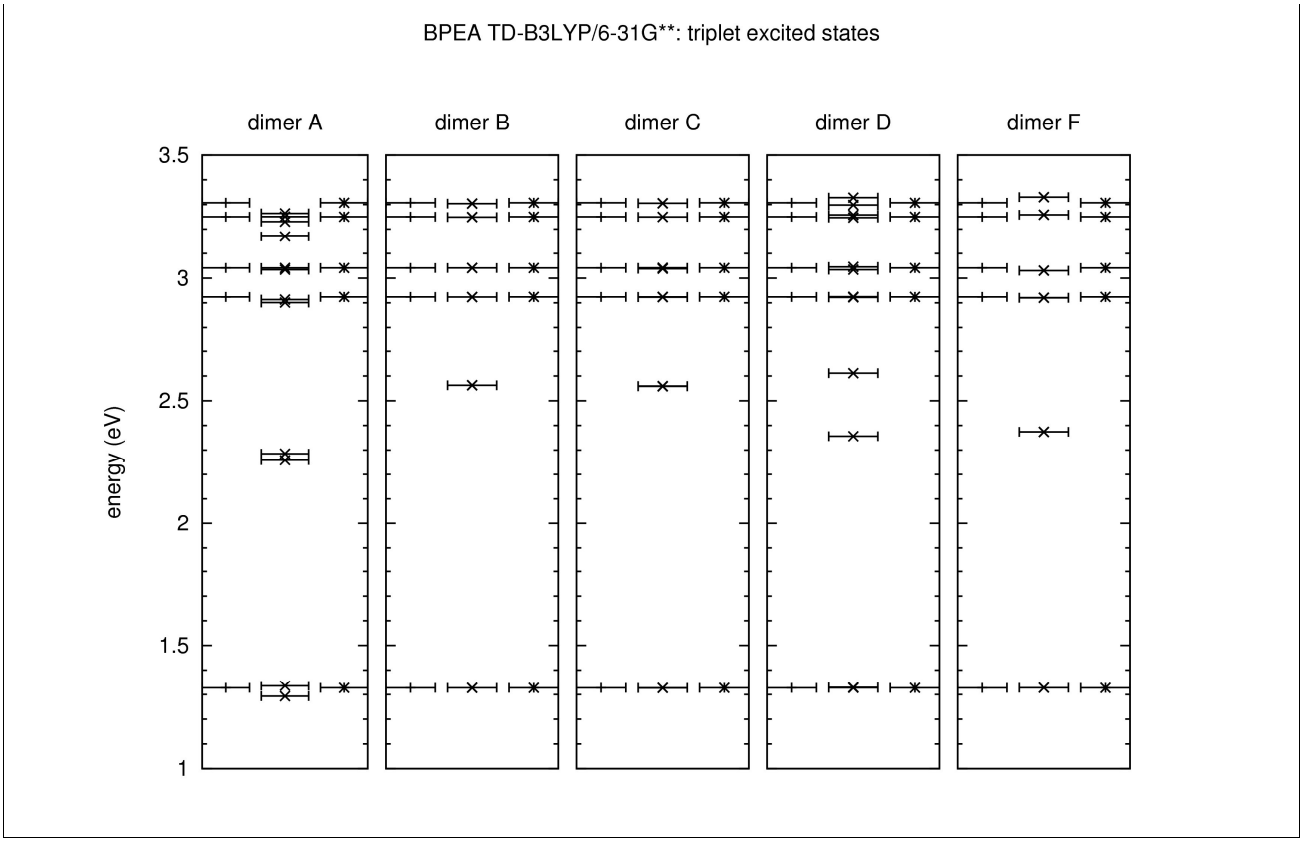
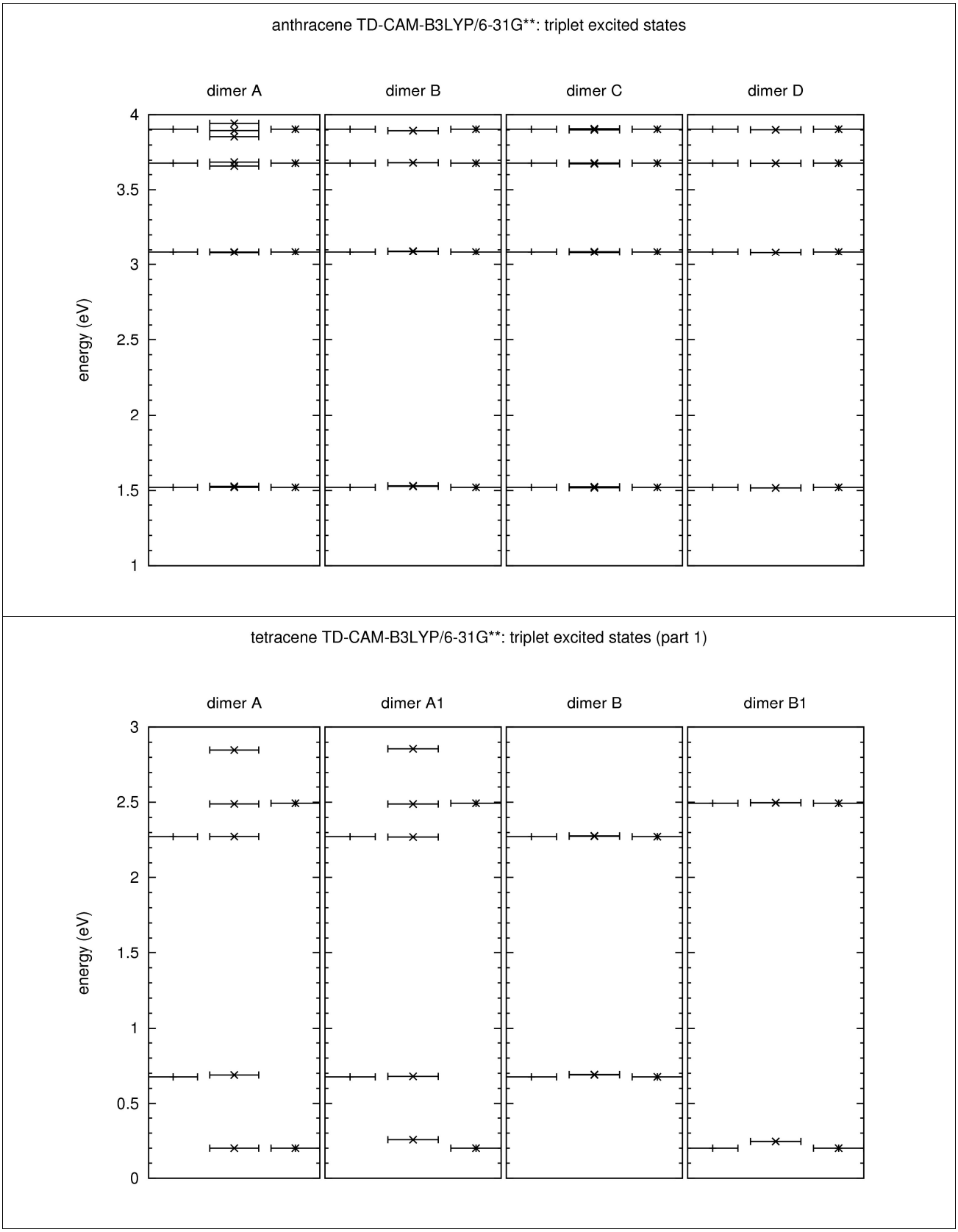
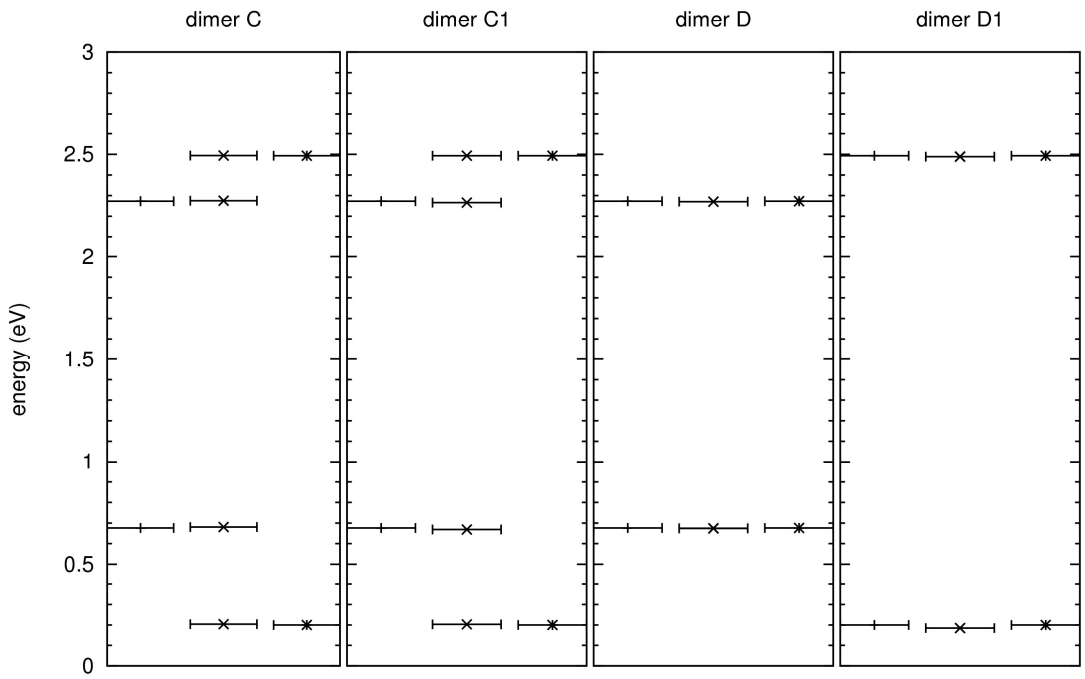


Fig. SI16: TD-CAM-B3LYP/6-31G TRIPLET EXCITED STATES**



tetracene TD-CAM-B3LYP/6-31G**: triplet excited states (part 2)



DPA TD-CAM-B3LYP/6-31G**: triplet excited states