Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Evaluation of Electronic Polarization energy in Oligoacene Molecular Crystals Using solvated supermolecular approach

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Table S1. Electronic Energies (E_0), Ionization Potential (IP), Electron Affinity (EA), and Polarization Energies ($P_{\pm}$) of naphthalene trimer models with a face-to-face distance range from 3.0 Å to 6.0 Å from BLW method and CDFT method.[a]

d	charge	BLW			CDFT		
		E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)	E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)
				trimer			
3.0	-1	-1157.079271	-0.613	-0.006	-1157.846438	-0.438	-0.091
	+1	-1156.846396	6.950	-0.862	-1157.607969	6.927	-0.978
	0	-1157.101786			-1157.862520		
3.2	-1	-1157.127199	-0.693	0.074	-1157.889209	-0.576	0.047
	+1	-1156.892493	7.080	-0.732	-1157.648204	7.134	-0.771
	0	-1157.152665			-1157.910360		
3.4	-1	-1157.152634	-0.744	0.125	-1157.911779	-0.653	0.124
	+1	-1156.916379	7.173	-0.639	-1157.668901	7.262	-0.643
	0	-1157.179966			-1157.935761		
3.6	-1	-1157.165916	-0.774	0.155	-1157.923895	-0.690	0.161
	+1	-1156.928190	7.243	-0.569	-1157.679357	7.344	-0.561
	0	-1157.194364			-1157.949246		
3.8	-1	-1157.173077	-0.790	0.171	-1157.930545	-0.705	0.176
	+1	-1156.933873	7.299	-0.512	-1157.684379	7.403	-0.502
	0	-1157.202114			-1157.956448		
4.0	-1	-1157.177190	-0.796	0.177	-1157.934648	-0.707	0.178
	+1	-1156.936496	7.346	-0.466	-1157.686839	7.450	-0.455
	0	-1157.206446			-1157.960621		
4.2	-1	-1157.179859	-0.797	0.178	-1157.937420	-0.702	0.174
	+1	-1156.937698	7.387	-0.425	-1157.688010	7.489	-0.416
	0	-1157.209150			-1157.963227		
4.4	-1	-1157.181838	-0.793	0.174	-1157.939117	-0.697	0.168
	+1	-1156.938248	7.422	-0.390	-1157.688247	7.523	-0.382
	0	-1157.210986			-1157.964728		
4.6	-1	-1157.183444	-0.788	0.169	-1157.940125	-0.691	0.163
	+1	-1156.938496	7.454	-0.358	-1157.687946	7.554	-0.352
	0	-1157.212420			-1157.965533		
4.8	-1	-1157.184745	-0.782	0.163	-1157.940875	-0.685	0.156
	+1	-1156.938525	7.482	-0.330	-1157.687517	7.579	-0.326
	0	-1157.213468			-1157.966055		
5.0	-1	-1157.185896	-0.775	0.156	-1157.941369	-0.680	0.152
	+1	-1156.938486	7.508	-0.304	-1157.686938	7.604	-0.301
	0	-1157.214384			-1157.966366		
5.2	-1	-1157.186821	-0.768	0.149	-1157.941874	-0.675	0.146
	+1	-1156.938314	7.530	-0.281	-1157.686445	7.625	-0.280

	0	-1157.215042			-1157.966672		
5.4	-1	-1157.187613	-0.761	0.142	-1157.942319	-0.669	0.140
	+1	-1156.938089	7.551	-0.261	-1157.685947	7.645	-0.260
	0	-1157.215585			-1157.966904		
5.6	-1	-1157.188311	-0.754	0.135	-1157.942857	-0.663	0.134
	+1	-1156.937844	7.570	-0.242	-1157.685589	7.664	-0.241
	0	-1157.216035			-1157.967228		
5.8	-1	-1157.188854	-0.748	0.129	-1157.943302	-0.657	0.128
	+1	-1156.937523	7.587	-0.225	-1157.685196	7.681	-0.225
	0	-1157.216340			-1157.967451		
6.0	-1	-1157.189354	-0.742	0.123	-1157.943722	-0.651	0.122
	+1	-1156.937218	7.603	-0.209	-1157.684831	7.696	-0.209
	0	-1157.216613			-1157.967652		
				single			
	-1	-385.716656	-0.619		-385.970312	-0.529	
	+1	-385.452333	7.812		-385.699234	7.905	
	0	-385.739404			-385.989741		

[a]The optimized geometry of neutral naphthalene at B3LYP/6-311G(d,p) level.

Table S2. Electronic Energies (E_0), Ionization Potential (IP), Electron Affinity (EA), and Polarization Energies ($P_{\pm}$) of the face-to-face orientation of naphthalene trimer model with dielectric constant (ε) from BLW method and CDFT method.[a]

		BLW			CDFT		
ε	charge	E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)	E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)
1.50	-1	-1157.199265	-0.268	-0.351	-1157.972657	0.077	-0.606
	+1	-1156.959083	6.804	-1.008	-1157.717516	6.866	-1.039
	0	-1157.209129			-1157.969839		
2.00	-1	-1157.210451	-0.002	-0.617	-1157.993278	0.494	-1.023
	+1	-1156.970588	6.529	-1.283	-1157.733248	6.582	-1.323
	0	-1157.210540			-1157.975116		
2.75	-1	-1157.219681	0.216	-0.835	-1158.011174	0.853	-1.382
	+1	-1156.980119	6.303	-1.509	-1157.746358	6.354	-1.551
	0	-1157.211732			-1157.979844		
4.00	-1	-1157.227427	0.399	-1.018	-1158.026943	1.165	-1.694
	+1	-1156.988150	6.112	-1.700	-1157.757472	6.167	-1.738
	0	-1157.212753			-1157.984114		
8.00	-1	-1157.236008	0.601	-1.220	-1158.045377	1.528	-2.057
	+1	-1156.997083	5.900	-1.912	-1157.769924	5.967	-1.938
	0	-1157.213906			-1157.989217		

[a]The optimized geometry of neutral naphthalene at B3LYP/6-311G(d,p) level.

Table S3. Calculated Ionization Potential (IP), Electron Affinity (EA) of gas and solid phase for face-to-face parallel multimers. xM-paral. models mean an excess charge is located on x-2 center molecules combined with two explicitly neutral molecules.[a]

Method	Model	IPg	EAg	IPc	EAc
B3LYP	3M-paral	7.812	-0.619	6.303	0.216
	4M-paral	7.061	-0.204	5.885	0.569
	5M-paral	6.691	-0.009	5.708	0.704
	6M-paral	6.458	0.123	5.606	0.780
CAM-B3LYP	3M-paral	8.026	-0.567	6.512	0.267
	4M-paral	7.497	-0.372	6.317	0.401
	5M-paral	7.238	-0.317	6.233	0.441
	6M-paral	7.088	-0.290	6.198	0.445

[a]The optimized geometry of neutral naphthalene at B3LYP/6-311G(d,p) level.

Table S4. Electronic Energies (E_0), Ionization Potential (IP), Electron Affinity (EA), and Polarization Energies ($P_\pm$) of oligoacenes various model from BLW method.[a]

	charge	gas-phase			solid-phase		
		E_0 (a.u.)	IP/EA (eV)	$P_\pm$ (eV)	E_0 (a.u.)	IP/EA (eV)	$P_\pm$ (eV)
				Naphthalene			
1M	-1	-385.561548	-0.748		-385.612689	0.571	-1.319
	+1	-385.302077	7.808		-385.348786	6.610	-1.198
	0	-385.589021			-385.591699		
5M	-1	-1927.907577	-0.653	-0.095	-1927.951980	0.319	-1.067
	+1	-1927.662840	7.312	-0.496	-1927.702788	6.462	-1.346
	0	-1927.931557			-1927.940249		
9M	-1	-3470.244027	-0.514	-0.234	-3470.283594	0.245	-0.993
	+1	-3469.997504	7.223	-0.585	-3470.037610	6.449	-1.359
	0	-3470.262927			-3470.274603		
				Anthracene			
1M	-1	-539.243889	0.120				
	+1	-538.981021	7.033				
	0	-539.239488					
5M	-1	-2696.184603	0.226	-0.106	-2696.231613	1.173	-1.053
	+1	-2695.935034	6.565	-0.468	-2695.976121	5.780	-1.253
	0	-2696.176306			-2696.188524		
				Tetracene			
1M	-1	-692.731232	0.687				
	+1	-692.467341	6.494				
	0	-692.705978					
5M	-1	-3463.526836	0.740	-0.053	-3463.575543	1.659	-0.972
	+1	-3463.278989	6.004	-0.490	-3463.321590	5.251	-1.243
	0	-3463.499639			-3463.514567		
				Pentacene			
1M	-1	-846.464710	1.210				
	+1	-846.196924	6.076				
	0	-846.420229					
5M	-1	-4231.840714	1.286	-0.076	-4231.893853	2.205	-0.995
	+1	-4231.586881	5.621	-0.455	-4231.631172	4.942	-1.134
	0	-4231.793462			-4231.812804		

[a]Molecular crystal geometries were obtained from oligoacene crystals.

Table S5. Electronic Energies (E_0), Ionization Potential (IP), Electron Affinity (EA), and Polarization Energies ($P_{\pm}$) of naphthalene various model from CDFT method.[a]

	charge	gas-phase			solid-phase		
		E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)	E_0 (a.u.)	IP/EA (eV)	$P_{\pm}$ (eV)
1M	0	-385.840075			-385.844696		
	-1	-385.815952	-0.656		-385.874592	0.814	-1.470
	1	-385.549676	7.902		-385.606634	6.478	-1.424
5M	0	-1929.198399			-1929.217745		
	-1	-1929.177189	-0.577	-0.079	-1929.245597	0.758	-1.414
	1	-1928.924565	7.451	-0.451	-1928.984577	6.345	-1.557
9M	0	-3472.552789			-3472.584617		
	-1	-3472.536472	-0.444	-0.212	-3472.613163	0.777	-1.433
	1	-3472.281969	7.369	-0.533	-3472.352350	6.320	-1.582

[a]Molecular crystal geometries were obtained from crystal structures of naphthalene.

Table S6. Ionization Potential (IP), Electron Affinity (EA) of gas and solid phase of oligoacenes obtained from the solvated 5M model and compare with experimental values.[a]

	IPg	EAg	IPc	EAc
		CAM-B3LYP		
Naphthalene	8.035	-0.685	6.695	0.385
Anthracene	7.271	0.169	6.021	1.227
Tetracene	6.735	0.742	5.493	1.722
Pentacene	6.301	1.269	5.169	2.279
		BLYP		
Naphthalene	7.645	-0.777	6.298	0.289
Anthracene	6.859	0.093	5.605	1.141
Tetracene	6.318	0.648	5.077	1.614
Pentacene	5.915	1.162	-	-
		B3LYP		
Naphthalene	7.808	-0.748	6.462	0.319
Anthracene	7.033	0.120	5.780	1.173
Tetracene	6.494	0.687	5.251	1.659
Pentacene	6.076	1.210	4.942	2.205
		exp.		
Naphthalene	8.12[b]	0.15[c]	6.40[b]	1.10[d]
Anthracene	7.36[b]	0.60[e]	5.70[b]	1.70[f]
Tetracene	6.90[b]	0.88[g]	5.25[h]	1.80[d]
Pentacene	6.58[b]	1.35[c]	4.85[b]	2.40[f]

[a]Molecular crystal geometries were obtained from oligoacene crystals.

[b]Ref 1. [c]Ref 2. [d]Ref 3. [e]Ref 4. [f]Ref 5. [g]Ref 6. [h]Ref 7.

References

1. N. Sato, K. Seki and H. Inokuchi, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1621-1633.
2. R. S. Ruoff, K. M. Kadish, P. Boulas and E. C. M. Chen, *J. Phys. Chem.*, 1995, **99**, 8843-8850.
3. K. H. Frank, P. Yannoulis, R. Dudde and E. E. Koch, *J. Chem. Phys.*, 1988, **89**, 7569-7576.
4. S. Chowdhury, T. Heinis and P. Kebarle, *J. Am. Chem. Soc.*, 1986, **108**, 4662-4663.
5. P. E. Schwenn, P. L. Burn and B. J. Powell, *Org. Electron.*, 2011, **12**, 394-403.
6. E. C. M. Chen and W. E. Wentworth, *Mol. Cryst. Liq. Cryst. Incorporating Nonlinear Opt.*, 1989, **171**, 271-285.
7. M. Pope, J. Burgos and J. Giachino, *J. Chem. Phys.*, 1965, **43**, 3367-3371.