

Supporting Information for  
**Ionization Energies, Electron Affinities, and Polarization Energies of Organic  
Molecular Crystals: Quantitative Estimations from a Polarizable Continuum  
Model (PCM)–Tuned Range-Separated Density Functional Approach**

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## Computational Details

In this work, in the search for optimal range-separation  $\omega$  values, we have employed a homemade script, “**xtune\_09.py**”, which is available through request to the authors. This script implements the “Golden proportion” method based on Brent’s algorithm in Python.<sup>1</sup> We employed this method to calculate accurate  $\omega$  values while having to take account of a lesser number of single-point calculations compared to the conventional fitting approach. The internal options IOp(3/107) and IOp(3/108) of the Gaussian software were utilized to set the  $\omega$  values for RS functionals. The optimal  $\omega$  values were searched in the range of  $0.001 \sim 0.50$  Bohr<sup>-1</sup>. For help and further details, turn to “**xtune\_09.py -h**”.

For  $\omega$  tuning of gas-phase molecules, the first step is to create a Gaussian input file (*i.e.*, molecule.gjf) including the information below. The second step is to run “**xtune\_09.py molecule.gjf**”. After the tuning process is completed, the script will automatically generate a new input file including the optimal  $\omega$ . Finally, it is a matter of performing the SCF calculations based on the new input file to evaluate the HOMO and LUMO energies.

```
%chk=pentacene.chk
%nprocshared=16
%mem=8GB
#p lc-wpbe/may-cc-pvdz      (define RS functional and basis set)

title

0 1
6      6.142703    0.716746   -0.000042
6      6.142691    -0.716741   -0.000044
6      4.957244    -1.415307   -0.000011
6      3.694822    -0.730605   0.000040
...
1      -7.096181   -1.253171   -0.000021
1      -7.096180   1.253153    0.000104
1      -4.954416   2.510372    0.000011
```

For  $\omega$  tuning of a molecular crystal with PCM, the first step is to create a Gaussian input file (*i.e.*, crystal.gjf) including the information below. Apply then the same procedure as described above.

```

%chk=pentacene-pcm.chk
%nprocshared=16
%mem=8GB
#p lc-wpbe/may-cc-pvdz scrf(pcm,read)      (add PCM keyword)

title

0 1
6       6.142703   0.716746   -0.000042
6       6.142691   -0.716741   -0.000044
6       4.957244   -1.415307   -0.000011
6       3.694822   -0.730605   0.000040
6       3.694805   0.730575   0.000039
...
1     -4.954310   -2.510341   0.000049
1     -2.475544    2.510277   -0.000066
1     -2.475676   -2.510308   -0.000111
1     -0.000100    2.511135   0.000056

eps=3.6          (define the specific dielectric constant of crystal)

```

We first tested the effect of extending the basis set from cc-pVDZ to may-cc-pVDZ and aug-cc-pVDZ for pentacene and C<sub>60</sub>. We found that the may-cc-pVDZ basis achieve the best balance between accuracy and computational cost.

**Table S1.** Effect of basis sets on the calculated parameters for pentacene and C<sub>60</sub>. All values are in eV.

(Pentacene)	$\omega^*$	IE (- $\varepsilon_H$ )	EA (- $\varepsilon_L$ )	$E_g$
cc-pVDZ	0.194	6.28	1.34	4.94
May-cc-pVDZ	0.187	6.35	1.49	4.86
Aug-cc-pVDZ	0.186	6.33	1.50	4.83

(C <sub>60</sub> )	$\omega^*$	IE (- $\varepsilon_H$ )	EA (- $\varepsilon_L$ )	$E_g$
cc-pVDZ	0.204	7.85	2.28	5.57
May-cc-pVDZ	0.183	7.83	2.47	5.36
Aug-cc-pVDZ	0.180	7.80	2.48	5.32

We then performed the  $\omega$  tuning in the framework of the PCM and conductor-like-PCM (C-PCM) models. We calculated the transport gap,  $E_g$ , of pentacene at the LC- $\omega$ PBE\*/may-cc-pVDZ level. Since there is hardly any difference between the PCM and C-PCM results, we chose to keep using the default PCM approach.

**Table S2.** Pentacene crystal: Results with the PCM and Conductor-like-PCM (C-PCM) models at the LC- $\omega$ PBE\*/may-cc-pVDZ level.  $E_g$  denotes the transport gap (IE – EA). All values are in eV.

Models	$\omega^*$	IE ( $-\epsilon_H$ )	EA ( $-\epsilon_L$ )	$E_g$
PCM	0.0463	5.14	2.66	2.48
C-PCM	0.0461	5.17	2.69	2.48

**Table S3.** Calculated energies (in eV) as a function of dielectric constant  $\epsilon$  (from 1.5 to 8.5).

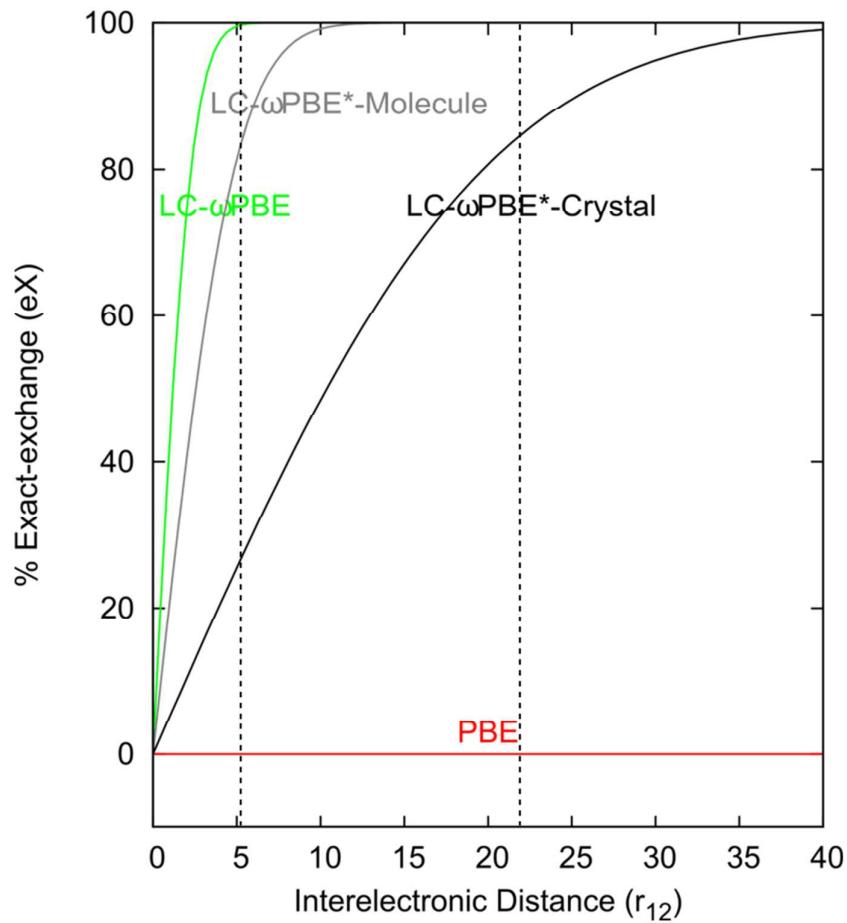
$\epsilon$	$\omega^*$	IE ( $-\epsilon_H$ )	EA ( $-\epsilon_L$ )	$E_g$
Pentacene				
1.5	0.103	5.76	2.01	3.75
2.5	0.063	5.34	2.44	2.90
3.6	0.046	5.14	2.66	2.48
3.94	0.044	5.11	2.70	2.41
4.5	0.040	5.07	2.75	2.32
5.5	0.035	5.01	2.82	2.19
8.5	0.030	4.94	2.92	2.02
TIPS-pentacene				
1.5	0.086	5.58	2.45	3.13
2.5	0.054	5.25	2.81	2.44
3.6	0.041	5.11	2.99	2.12
4.5	0.036	5.05	3.08	1.97
5.5	0.032	5.01	3.15	1.86
8.5	0.025	4.94	3.26	1.68

**Table S4.** Calculated  $-\epsilon_H$ ,  $-\epsilon_L$ , and  $E_g$  values for a series of organic molecular crystals at the LC- $\omega$ PBE\*/may-cc-pVDZ level using different methods; the mean absolute deviation (MAD) values are also listed in comparison to GW and experimental data. All values are in eV.

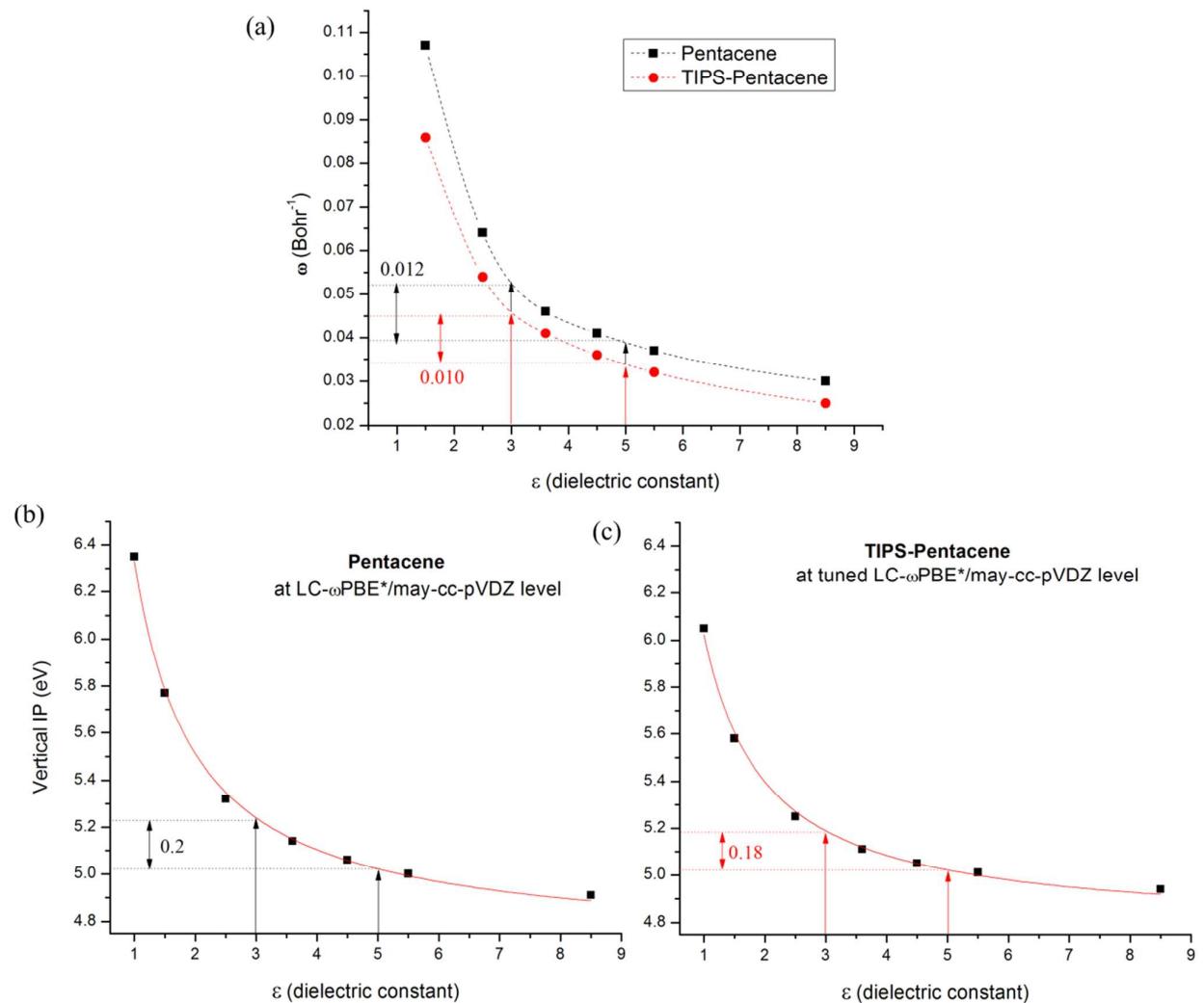
Methods	Gas tuning			Gas tuning + PCM			PCM tuning + PCM		
	$-\epsilon_H$	$-\epsilon_L$	$E_g$	$-\epsilon_H$	$-\epsilon_L$	$E_g$	$-\epsilon_H$	$-\epsilon_L$	$E_g$
Pentacene	6.35	1.49	4.86	6.39	1.53	4.86	5.14	2.66	2.48
TIPS-pentacene	6.03	2.04	3.99	6.10	2.12	3.98	5.11	2.99	2.12
PTCDA	8.14	3.07	5.07	7.88	2.83	5.05	6.62	3.92	2.70
Rubrene	6.19	1.38	4.81	6.28	1.48	4.80	5.30	2.39	2.91
$C_{60}$	7.83	2.47	5.36	7.72	2.37	5.35	6.20	3.62	2.58
$C_{60}$ PCBM	7.28	2.30	4.98	7.30	2.32	4.98	5.89	3.50	2.39
$C_{70}$	7.66	2.51	5.15	7.56	2.41	5.15	6.13	3.63	2.50
$C_{70}$ PCBM	7.02	2.44	4.58	7.00	2.43	4.57	5.84	3.50	2.34
MAD (vs. GW)	1.46	1.29	2.39	<b>1.43</b>	<b>1.32</b>	<b>2.38</b>	<b>0.04</b>	<b>0.25</b>	<b>0.13</b>
MAD (vs. Exp)	1.51	1.50	2.63	<b>1.45</b>	<b>1.47</b>	<b>2.63</b>	<b>0.12</b>	<b>0.29</b>	<b>0.25</b>

**Table S5.** Calculated  $-\epsilon_H$ ,  $-\epsilon_L$ , and  $E_g$  values for various molecules and crystals at the PBE/may-cc-pVDZ level; the mean absolute deviation (MAD) values are also listed by comparison to GW and experimental data. All values are in eV.

PBE	Gas-phase Molecule			Solid-state Crystal ( <i>plus</i> PCM)		
	$-\epsilon_H$	$-\epsilon_L$	$E_g$	$-\epsilon_H$	$-\epsilon_L$	$E_g$
Pentacene	4.43	3.29	1.14	4.47	3.33	1.14
TIPS-pentacene	4.44	3.52	0.92	4.41	3.49	0.92
Rubrene	4.49	3.02	1.47	4.57	3.11	1.46
PTCDA	6.25	4.79	1.46	5.99	4.54	1.45
C <sub>60</sub>	5.84	4.21	1.63	5.73	4.10	1.63
C <sub>60</sub> PCBM	5.28	3.81	1.47	5.32	3.86	1.46
C <sub>70</sub>	5.72	4.01	1.71	5.64	3.94	1.70
C <sub>70</sub> PCBM	5.35	3.77	1.58	5.36	3.79	1.57
MAD (vs. GW)	1.54	1.43	3.22	<b>0.53</b>	<b>0.45</b>	<b>1.12</b>
MAD (vs. Exp)	1.91	1.39	3.31	<b>0.57</b>	<b>0.37</b>	<b>0.86</b>



**Figure S1.** Percentage of exact exchange included as a function of interelectronic distance for the various functionals. Tuned variants ( $\omega^*$ ) for pentacene.



**Figure S2.** Evolutions as a function of dielectric constant of: (a) optimal  $\omega$  values and vertical IE ( $-\epsilon_H$ ) of pentacene (b) and TIPS-pentacene (c), at the optimally tuned LC- $\omega$ PBE\*/may-cc-pVDZ level.

## References

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4. Li, T.; Balk, J.W.; Ruden, P.P.; Campbell, I.H.; Smith, D.L. Channel formation in organic field-effect transistors, *J. Appl. Phys.* 2002, **91**, 4312–4318.