Electronic Supplementary Material (ESI) for Chemical Science. This journal is © The Royal Society of Chemistry 2017

Towards a Full Understanding of Regioisomer Effects of Indene-C₆₀ Bisadduct Acceptors in Bulk Heterojunction Polymer Solar Cells

Tiantian Cao,^a Ning Chen,^{*a} Guangxin Liu,^a Yingbo Wan,^b José Darío Perea,^c Yijun Xia,^b Zhaowei Wang, ^a Bo Song,^b Ning Li,^{*c} Xiaohong Li,^{*b} Yi Zhou,^{*a} Christoph J. Brabec^{cd} and Yongfang Li^a

^a Laboratory of Advanced Optoelectronic Materials, College of Chemistry Chemical Engineering and Materials Science, Soochow University Suzhou 215123, China. E-mail: chenning@suda.edu.cn; yizhou@suda.edu.cn

^b Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry Chemical Engineering and Materials Science, Soochow University Suzhou 215123, China. E-mail: lxh83@suda.edu.cn.

^c Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany. E-mail: ning.li@fau.de

^d Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058, Erlangen, Germany.

1. The third stage separation of ICBA



Figure S1. HPLC chromatography of $IC_{60}BA$ -m ($IC_{60}BA$ mixture). Conditions: Buckyprep-D column (10 × 250 mm); eluent, toluene; flow rate, 2 mL/min; detection, 310 nm.

2. NMR Characterization of ICBA-m

The ¹H chemical shifts of C_{60} bisadducts got affected by the attaching position of the substituents. Thus it could be very helpful to determine which isomeric structures presented in the samples with mixtures only based on their NMR chemical shifts, especially with the cases as IC₆₀BA when separating the mixtures of isomers is very difficult to accomplish.

In Figure S2, the ¹H NMR of expanded region for c/c'/c"/c", 17 pairs of peaks were assigned to the indene substituents, while peak-1 was easily identified from the symmetric isomer *trans*-1. According to previous report, the chemical shift of c, c', c", c"' would be noticeably shielded and decreased in the order of *trans*-1, *trans*-2, *trans*-3, *trans*-4, *e*.¹ Thus the peak pairs-2,3,4,5 were expected to come from *trans*-2; the peak pairs-6,7,8,9 were from *trans*-3; the peak pairs-10,11,12,13 were from *trans*-4 and peak pairs-14,15,16,17 were from *e*. Furthermore, in order to confirm our prediction from the NMR analysis of the IC₆₀BA mixture, a combined investigation based on HPLC separation and UV-Vis characterization were employed to unambiguously identify every isomeric structures in the mixture.



Figure S2. 600 MHz c, c', c", c"' selected region of ¹H 1D-NMR spectra of IC₆₀BA in CDCl₃.

Substituents position	# of δ for c/c'/c''/c'''	# of δ for d/d'/d''/d'''
<i>cis</i> -1 (<>)	2	2
<i>cis</i> -1 (><)	2	2
<i>cis</i> -1 (<>)	4	4
cis-2 (<>)	2	2
cis-2 (><)	2	2
cis-2 (<>)	4	4
cis-3 (<>)	2	2
<i>cis</i> -3 (><)	2	2
cis-3 (<>)	4	4
trans-1 (<>/><)	1	2
trans-1 (<>)	1	2
trans-2 (<>)	2	2
trans-2 (><)	2	2
trans-2 (<>)	4	4
trans-3 (<>)	2	2
trans-3 (><)	2	2
trans-3 (<>)	4	4
trans-4 (<>)	2	2
trans-4 (><)	2	2
trans-4 (<>>)	4	4
<i>е</i> -1 (_Т)	4	4
<i>e</i> -2 (┘└)	4	4

Table S1. Theoretical numbers of chemical shifts for c/c' and d/d' region of $IC_{60}BA$ regioisomers.*

* The CH₂ groups on the two indene substituents faced towards each other denoted as < < or against each other denoted as < > or faced to the same side denoted as <</>>, for*e* $isomers, denoted as <math>_{1\Gamma}$ and JL , respectively.

Table S2. The list of ¹H NMR chemical shifts of c and d regions for $IC_{60}BA$ isomers.

Isomor	Assignment(d/d'/d''/d''')	Assignment (c/c'/c''/c''')
isomer	¹ H (ppm)	¹ H (ppm)
trans-1	3.91	5.24
	3.03	5.24
	4.05	5.11
trans-2(a)	3.00	5.00
	3.54	5.01
	2.82	4.81
trans-2(h)	4.04	5.10
ti ulis-2(b)	2.97	4.95
trans-2(c)	3.57	5.02
	2.85	4.87

	3.83	4.95
	2.83	4.67
trans-3(a)	3.48	4.90
	2.71	4.51
trans-3(h)	3.79	4.95
	2.81	4.60
trans-3(c)	3.47	4.89
	2.72	4.57
	3.57	4.85
trans-4(a)	2.77	4.69
	3.22	4.77
	2.61	4.53
trans-4(h)	3.38	4.85
	2.71	4.63
trans-4(c)	3.54	4.76
	2.70	4.61
	3.48	4.62
<i>e</i> -1	2.66	4.43
	3.26	4.56
	2.64	4.51
	3.55	4.58
P-7	2.69	4.54
	3.32	4.52
	2.50	4.00

Figure S3 is the selective region of ¹H-¹H gCOSY spectra c, c', c", c"' and d, d', d", d"'. For IC₆₀BA, the chemical shifts of d and d' (d" and d'") are always different since one of them is pointing towards the fullerene ball while the other is away, which gave them different electronic environments, the chemical shifts of c and c' (c" and c"") are different in asymmetrical structures. Thus except for the *trans*-1 isomers, four cross-peaks came from c/c' to d/d' or c"/c"' to d"/d"' can be seen in ¹H-¹H 2D-gCOSY spectrum. Like the shifts 2 and 2' of c, c', c", c"' region each showed two cross-peaks with the shifts 2 and 2' of d, d', d", d"' region. In the *trans*-1 isomers, c/c'/c"/c"' gave one chemical shift, so there would be two cross-peaks like the signal 1 of c, c', c", c"' region with the shifts 1 and 1' of d, d', d", d"' region. Therefore, shifts 1 in c/c'/c"/c"' region came from indene substituents of trans-1 isomers while shifts 2/2' through 17/17' came from the other 16 types of indene substituents of IC₆₀BA isomers.



Figure S3. Selected region of the ¹H-¹H gCOSY spectra of IC₆₀BA in CDCl₃

In ¹H {¹³C} gHSQC, where the correlations from protons directly connected to carbons were detected, the CH2 groups from d, d', d", d", showed cross peaks in Figure S4-A with different phase of those for CH groups of c, c', c", c"' in Figure S4-B.

The CH₂ d and d' (d" and d"") are from the two chemically non-equivalent protons bonded to the same carbon. They provided seventeen pair of proton resonances in Figure S4-A, each shared the same chemical shift of the directly bound ¹³C. A total of 33 cross-peaks are resolved for c, c', c", c"' in Figure S3-B. According to the COSY spectrum, there was a *trans*-1 isomer in this mixture contributed only one shift for c/c'/c''/c''' because of the symmetric structure. The rest 32 cross-peaks would come from c/c' (c''/c''') of sixteen bi-indene substituents positioned other than *trans*-1 isomers.



Figure S4. Two dimensional ¹H {¹³C} gHSQC spectra of $C_{60}(CH_2)$ (Indene) in CDCl₃ ,with the selected region of d, d', d", d"' (A), and selected region of c, c', c", c"'(B).



Figure S5. HPLC purification process of the *trans*-3(a)-P, Conditions: Buckyprep-D column (10 i.d. × 250 mm) using toluene as eluent (flow rate 2 mL/min).

Figure S5 shows the HPLC process of the *trans*-3(a)-P. We collected B fraction and removed A, C fractions from *trans*-3(a) to get sample with higher purity, namely *trans*-3(a)-P.

For further investigating how the isomers affect the photovoltaic performance when they were used as acceptors in PSCs, we studied the percentage of 12 main isomers in mixture using integral method of NMR. Because the NMR spectra of c/c'/c''/c''' region is much simpler than that of d/d'/d''/d''' region and much easier to distinguish, we utility the NMR spectra of c/c'/c''/c''' region to obtain the percentage of 12 main isomers in IC₆₀BA mixture.

As shown in Figure S6, many peaks were overlapped, in order to get a relatively precise integral value, we divided the spectra into several integral parts, which were separated from others and indicated by alphabet $A \sim P$ with a square. The integral values of each part were listed in Table S3. The digits represent the 2 hydrogen atoms of c/c'/c''' region of equivalent indene and their attributions were listed in Table S4.



Figure S6. Enlarged partial view of the NMR spectra of c/c'/c''/c''' region of IC₆₀BA mixture. **Table S3.** Integral value of each integral part in the NMR spectra of c/c'/c''/c''' region of IC60BA mixture

Integral part	Integral value
А	27.04
В	46.80
С	69.75
D	117.04
E	96.70
F	23.32
G	33.50
н	24.01
I.	30.71
J	21.17
К	49.35
L	120.96
М	117.00
Ν	157.18
0	38.82
Р	26.65

Structure	Attribution
trans-1	1
trans-2(a)	2, 5
trans-2(b)	3
trans-2(c)	4
<i>trans</i> -3(a)	6, 9
<i>trans</i> -3(b)	7
trans-3(c)	8
trans-4(a)	10, 13
<i>trans</i> -4(b)	11
trans-4(c)	12
<i>e</i> -1	14, 16
<i>e</i> -2	15, 17

Table S4. The attribution of the peaks in the NMR spectra of c/c'/c''/c''' region of IC₆₀BA mixture.

_

Based on the above all, we get the formulas for calculating the integral value of 2 hydrogen atoms of c/c'/c''/c''' region of IC60BA according to the specific properties of each isomer: trans-1=A/2; trans-2(a)=H*2; trans-2(b)=B-H; trans-2(c)=F; trans-3(a)=K*2; trans-3(b)=D-(B-H)-K; trans-3(c)=E-K; trans-4(a)=J*2; trans-4(b)=G-J; trans-4(c)=I-J; e1=O*2; e2=P*2.

The percentage of each isomer hereto could be figured out by substituting the integral value in table into these formulas, as shown in Table S5.

Table S5. The percentage of each isomer in IC₆₀BA mixture.

Structure	The integral value of 2 hydrogen atoms of	Perce	entage (%)	
Structure	c/c'/c''/region			
trans-1	13.52	2.74	2.74	
trans-2(a)	48.02	9.73		
<i>trans</i> -2(b)	22.79	4.62	19.07	
trans-2(c)	23.32	4.72		
trans-3(a)	98.70	19.99		
trans-3(b)	44.90	9.09	38.67	
trans-3(c)	47.35	9.59		
trans-4(a)	42.34	8.58		
<i>trans</i> -4(b)	12.33	2.50	13.01	
<i>trans</i> -4(c)	9.54	1.93		
<i>e</i> -1	77.64	15.72	26 51	
<i>e</i> -2	53.30	10.79	20.51	



Figure S7. The percentage of each isomer in $IC_{60}BA$ mixture synthesized and the commercially available samples from Sigma and One materials.



Figure S9. (a) *J-V* curve of P3HT: IC₆₀BA *trans*-3(a), measured under an illumination of AM 1.5G, 100mW/cm², (b) IPCE spectra of device based on P3HT and *trans*-3(a).

3. AFM height image of IC₆₀BA



Figure S10. AFM height image $(2\mu m \times 2\mu m)$ of a) P3HT/trans-1, b) P3HT/trans-2(a), c) P3HT/trans-2(b), d) P3HT/trans-2(c), e) P3HT/IC₆₀BA-m, f) P3HT/trans-3(a), g) P3HT/trans-3(b), h) P3HT/trans-3(c), i) P3HT/trans-4(a), j) P3HT/trans-4(b), k) P3HT/trans-4(c), l) P3HT/e-1, m) P3HT/e-2 blend films.

4. Electron Mobility



Figure S11. J-V characteristics of electron-only devices based P3HT: IC₆₀BA isomers

5. Solubility studies of IC₆₀BA

We have theoretically characterized ICBA-*trans*-a, ICBA-*trans*-b and ICBA-*trans*-c with a fast and accurate combined first principles quantum mechanics with an external mathematical tool based on artificial neural networks (ANN). ANN transforms the molecular surface charge density distribution (sigma-profile) as determined by density functional theory (DFT) calculations within the framework of a continuum solvation model into solubility parameters. The 3D structures of the ICBA-*trans*-a, ICBA-*trans*-b and ICBA*trans*-c-fullerene considered in this study were built using HyperChem Professional 7, which calculates the most stable conformational structures under the force field method. Molecular geometries were optimized by TURBOMOLE 6.3 quantum chemical program package using high quality quantum chemical ab - initio electronic structure optimization on the BP-TZVP gas phase level. Sigma moments of molecules were calculated with COSMOtherm13 software using BP-TZVP-C21-1401 parameterization. COSMO-RS sigma moments as quantitative structure property relationships (QSPRs) are used as the five input values for the Artificial Neural Network Toolbox of MATLAB (R2010b). For the determination of relative solubilities, the total solubility distance (R_a), the intermolecular parameter of Flory-Huggins (χ) and the chemical potential of the mixture (μ_{mix}) were determined.

The disentanglement of the well-known Hildebrand solubility parameter δ_{τ} into the Hansen Solubility Parameters (HSPs) forms the basis for developing predictive solubility theories.² The Hildebrand solubility parameter is related to the density of the cohesive energy E_{τ} , which is defined as the increase in internal energy upon removal of the molecular interactions and can be thought as the energy required to fully separate a unit volume of molecules from the nearest neighbor when going into solution: ³

$$\delta_T = \sqrt{\frac{\Delta E_T}{V}}$$

(1)

where V is the molar volume. The Hildebrand theory predicts that molecules with similar δ_{τ} interact more closely, leading to improved miscibility. The later Hansen theory accounts for the fact that the cohesive forces in a liquid are not limited by only one type of interaction but are rather described by the combined effect of non-polar bonding (dispersive) forces, polar bonding (dipoledipole) forces and hydrogen bonding forces:³

 $E_T = E_d + E_p + E_{hb}, \tag{2}$

where E_d , E_p , and E_{hb} correspond to dispersive, polar and hydrogen bonding energies, respectively. Accordingly, the Hildebrand solubility parameter splits into the Hansen solubility parameters (HSPs) as:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_{hb}^2 \tag{3}$$

with

$$\delta_d^2 = \frac{\Delta E_d}{V}$$
$$\delta_p^2 = \frac{\Delta E_p}{V}$$
$$\delta_{hb}^2 = \frac{\Delta E_{hb}}{V}$$

· -



Figure S12. (A) (i) General visualization of the isomers ICBA. Lowest conformational molecular structures for the fullerenes: (A) (i) ICBA-*e*1 and (ii) ICBA-*e*2. (B) ICBA-*trans*-1 (i) –a and (ii) –b (C) ICBA-*trans*-2 (i) -a, (ii) -b and (iii) -c. (D) ICBA-*trans*-3 (i) -a, (ii) -b and (iii)-c. (E) ICBA-*trans*-4 (i) -a, (ii) -b and (iii) -c.

 δ_{hb} is the hydrogen bonding parameter, which becomes relevant in substances where hydrogen bonding to highly electronegative atoms is predominant. The polar parameter δ_p depends on the dipolar moment according to the Beerbower correlation.⁴ This term is particularly relevant when non-symmetrical molecules are considered. Finally, the non-polar contributions, mainly originating from dispersive interactions, are contained in the dispersion parameter δ_d , which is related to the enthalpy of vaporization of homomorphous bondings.⁵ We note that the Hansen theory is an approximation and that the molecular interactions can be more complex and thus underrepresented. Nevertheless, Hansen solubility parameter have been shown to provide a good estimation of the Flory-Huggins mixing parameter (χ) and thus generally allow reliable solubility predictions. ⁶

In the present work, upon structural molecular modeling of ICBA-*trans* (a, b and c) fullerenes (Figure S12) by calculating the lowest energy conformation structure using the force field method (HyperChem Professional⁷), we applied *ab-initio* density functional theory (DFT) to calculate the surface charge screening density σ (Figure S13) using the software package TURBOMOLE.⁸ COSMOtherm, which uses the conductor-like screening model for real solvents, short COSMO-RS,⁹ was then employed for calculating the σ -profile and the chemical potential (σ -potentials). Subsequently, we determined physical-chemistry structural

properties (σ -moments) using the previously established surface charge screening densities. We note that the σ -profile has no direct information on the van der Waals forces.

It therefore seems surprising that it might be possible to determine the HSPs based on the σ -profile. This is accomplished by utilizing the σ -moments as input for a computational technique that emulates the function of neuronal brain cells in human information processing, called artificial neural network (ANN). Here, ANN is proposed as a reliable alternative for the determination of HSPs. The software featuring ANN for predicting HSPs for a group of solvents was recently introduced by Jarvas et al. In order to predict Hansen solubility parameters from σ -moments with the help of ANN we use the weights of the interconnections, which have been previously established with a set of chemical compounds featuring a broad range of functional groups.^{10,11}

We now return to the computational procedure involving COSMO-RS. COSMO-RS was originally developed for studying the thermodynamic properties of solutions and mixtures based on computation of the chemical potential of a molecule in solution via statistical thermodynamics of interacting molecular surface segments.^{9, 12, 13} As opposed to the discrete model, which describes the molecular free energy of solvation as a sum of single solvent- solute point interactions (typically the basis for molecular dynamics calculations), COSMO- RS is based on a continuous, polarizable solvation medium, thereby reducing the number of interactions and thus the computational time. The basic idea of this approach is to represent the surface charge density σ of the real solvation in form of a molecular distribution called σ -profile ($P(\sigma)$) and consequently use $P(\sigma)$ in a regression function, relating material characteristics ($P(\sigma)$) to molecular properties, also referred to as quantitative structure property relationships (QSPR):

$$P_{s}^{X}(\sigma) = C_{0} + C_{1}M_{0}^{X} + C_{2}M_{1}^{X} + C_{3}M_{2}^{X} + C_{10}M_{hb,acc}^{X} + C_{14}M_{hb,don}^{X}$$
(4)

Where M_i^X is the i-th σ -moment of the solute X. The coefficients (C_X) can be derived by multilinear regression of the σ -moments using a reliable set of experimental data. Some of the σ -moments have a rather simple physical meaning. M_0^X represents the total surface area of the solute X, $M_0^X = M_{area}^X$ and M_1^X the electrostatic interaction energy (E.I) $M_1^X = M_{E.I}^X$, which is an estimation of the overall ability of the solute to interact electrostatically with a polarizable continuum. The third moment lacks a simple physical analogy and is best described as skewness of the σ -profile of the solute $M_2^X = M_{skew}^X$ which is directly related to the asymmetry of the σ -profile. The final terms $M_{hb,acc}^X$ and $M_{hb,don}^X$ quantify the ability of the solute to interact as a hydrogenbond acceptor and donor, respectively.⁹ Table S6 shows the five calculated basic σ -moments for the selected fullerenes in this work to illustrate the QSPRs involved in the regression and prediction process using ANN. We emphasize that full representation of the σ -profile (equation 4) may involve a wider range of σ -moments (Table S6). In Table S7 we illustrate the computed solubility parameters (Hildebrand parameter δ_T and the Hansen parameters $\delta_{dr}, \delta_{dr}, \delta_{hb}, \delta_{dr} + \delta_{hb}$ (MPa^{1/2}) for the twelve fullerenes employed

in this work: ICBA-*trans*-(1,2,3,4)a; ICBA-*trans*-(1,2,3,4)b; and ICBA-*trans*-(1,2,3,4)c. According to our chosen quantum method, the functional and the basis set, we used correspond to the parametrization BP-TZVP-C21-1014 that is required for the calculation of physicochemical data and contains intrinsic parameters of *COSM Otherm*13 as well as element-specific parameters for the *σ*-moments and finally the molar volume (Table S8).

Table S6. σ -moments (M_i^{χ}) for ICBA-*trans*-a, ICBA-*trans*-b and ICBA-*trans*-c calculated by COSMOtherm.

Molecule	Area (nm ²)	E. I.	Skew	Hb acc	Hb don
ICBA-trans-e1	5.8292	68.6964	-10.9181	0.0	0.0
ICBA-trans-e2	5.7341	67.8457	-10.6580	0.0	0.0

ICBA-trans-1ª	5.3369	72.5783	-40.7461	0.0	0.0
ICBA-trans-1b	5.6315	69.5822	-14.2289	0.0	0.0
ICBA-trans-2ª	5.6424	69.2980	-11.5335	0.0	0.0
ICBA-trans-2b	5.8279	69.7553	-11.1015	0.0	0.0
ICBA-trans-2c	5.8552	69.5190	-11.4464	0.0	0.0
ICBA-trans-3ª	5.5705	69.2353	-16.5044	0.0	0.0
ICBA- <i>trans</i> -3b	5.7626	69.2247	-10.9562	0.0	0.0
ICBA-trans-3c	5.5704	69.3844	-16.4721	0.0	0.0
ICBA-trans-4ª	5.6763	69.0191	-11.3788	0.0	0.0
ICBA- <i>trans</i> -4b	5.6852	69.3107	-11.2894	0.0	0.0
ICBA-trans-4c	5.6867	69.4951	-11.5431	0.0	0.0

E.I. : electrostatic interaction

Hb acc: Hydrogen bonding, acceptor

Hb don: Hydrogen bonding, donor

Table S7. Computed Hildebrand parameter δ_{τ} (Mpa^{1/2}) and Hansen parameters δ_d , δ_p , δ_{hb} , $\delta_p + \delta_{hb}$ (Mpa^{1/2}) for the fullerenes ICBAtrans-a; ICBA-trans-b; and ICBA-trans-c. (SPs: Solubility Parameters)

SPs	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
$\delta_{ au}$	21.32	21.27	21.08	21.27	21.26	21.76	21.34	21.26	21.29	21.26	21.26	21.27	21.27
δ_d	20.67	20.61	20.41	20.53	20.54	20.66	20.68	20.05	20.61	20.50	20.56	20.57	20.56
$\delta_{ ho}$	4.94	4.95	5.24	5.03	5.01	4.96	4.95	5.05	4.97	5.05	4.99	5.00	5.00
$\delta_{\scriptscriptstyle hb}$	1.71	1.78	0.78	2.32	2.19	1.86	1.79	2.41	1.92	2.43	2.09	2.10	2.14
$\delta_{ ho}$ + δ_{hb}	6.66	6.74	6.02	7.35	7.21	6.83	6.74	7.47	6.90	7.49	7.08	7.10	7.14

Table S8. Volume and molar volume for ICBA-trans-a, ICBA-trans-b and ICBA-trans-c calculated by BP-TZVP-30-1401 DFT.

Molecule	Volume (nm ³)	M_V (cm ³ /mol)
ICBA-trans-e1	0.9071	546.268
ICBA-trans-e2	0.8711	524.589
ICBA-trans-1a	0.8504	512.123
ICBA-trans-1b	0.8711	524.589
ICBA-trans-2a	0.8893	535.544
ICBA-trans-2b	0.9115	548.918
ICBA-trans-2c	0.9144	550.665
ICBA-trans-3a	0.8699	523.866
ICBA-trans-3b	0.9104	548.256
ICBA-trans-3c	0.8704	524.167
ICBA-trans-4a	0.9005	542.023
ICBA-trans-4b	0.9031	543.860
ICBA-trans-4c	0.8999	541.933



Figure S13. COSMO-RS visualization of the isomers ICBA: (A) ICBA-*e* (i) -1, (ii) -2. (B) ICBA-*trans*-1 (ii) –a and (ii) –b. (C) ICBA-*trans*-2 (ii) –a, (ii) –b and (iii) –c. (D) ICBA-*trans*-3 (ii) –a, (ii) –b and (iii) –c. I ICBA-*trans*-4 (ii) –a, (ii) –b and (iii) –c.

10 (eV) Eg (eV)	
3.84 1.62	
3.84 1.62	
3.74 1.42	
3.82 1.48	
	IO (eV) Eg (eV) 3.84 1.62 3.84 1.62 3.74 1.42 3.82 1.48

 Table S9.
 Molecular orbital energies for ICBA-trans-a, ICBA-trans-b and ICBA-trans-c calculated by BP-TZVP-30-1401 DFT.

ICBA-trans-2a	-5.44	-3.61	1.83
ICBA-trans-2b	-5.40	-3.90	1.50
ICBA-trans-2c	-5.41	-3.90	1.51
ICBA-trans-3a	-5.20	-3.71	1.49
ICBA-trans-3b	-5.44	-3.72	1.72
ICBA-trans-3c	-5.20	-3.71	1.49
ICBA-trans-4a	-5.47	-3.52	1.96
ICBA-trans-4b	-5.46	-3.47	1.93
ICBA-trans-4c	-5.49	-3.50	1.99

Table S10. Chemical potential for pure ICBA-trans-a, ICBA-trans-b and ICBA-trans-c calculated by BP-TZVP-30-1401 DFT.

μ(Kcal/mol)	<i>e</i> 1	e2	1a	1b	2a	2b	2c	За	3b	3c	4a	4b	4c
μ	-76.29	-75.46	-65.21	-71.82	-73.52	-75.90	-76.29	-70.80	-75.39	-70.74	-74.25	-74.25	-74.25

For solubility studies in the organic photovoltaic (OPV) device investigations and specially the accurate solvents choices for solar cells. It is convenient to introduce the solubility distance parameter, R_a , between two materials based on their respective partial solubility parameter. Ra predicts the differences between the Hansen parameters of a solvent ($\delta_{2,d}$, $\delta_{2,p}$, and $\delta_{2,hb}$) and the solute ($\delta_{1,d}$, $\delta_{1,p}$, and $\delta_{1,hb}$) as

$$R_{a} = \sqrt{4(\delta_{1,d} - \delta_{2,d})^{2} + (\delta_{1,p} - \delta_{2,p})^{2} + (\delta_{1,hb} - \delta_{2,hb})^{2}}$$
(5)

where the weighing factor 4 for the dispersion component was introduced by Hansen from empirical testing. The shorter the solute-solvent distance R_a in the HSP space, the higher the solubility. Good solubility is a decisive requirement for OPV cell processing.¹⁴ A series of halogenated solvents and non-halogenated was introduced in the HSPiP software and our determined HSP of ICBA-*trans*-a, ICBA-*trans*-b and ICBA-*trans*-c with the solubility limit set at 10mg/mL were introduced as the target. The determined solubility distances R_a of the selection of solvents are summarized in Table S11.

Table S11. Solubilit	y distance <i>R</i> _a in Mpa ^{1/2}	for ICBA-e, ICBA-trans-a,	ICBA-trans-b and ICBA-tr	ans-c in a selection of	f solvents
----------------------	--	---------------------------	--------------------------	-------------------------	------------

Solvents	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
Chlorobenzene	3.41	3.28	3.21	3.17	3.17	3.38	3.43	3.13	3.30	3.13	3.20	3.21	3.21
Chloroform	7.29	7.18	7.04	7.10	7.11	7.28	7.32	7.06	7.21	7.06	7.13	7.13	7.13
o-xyelene	7.10	6.99	7.11	6.84	6.86	7.06	7.11	6.79	6.99	6.79	6.89	6.90	7.89
Toluene	6.41	6.31	6.28	6.24	6.24	6.40	6.43	6.21	6.33	6.22	6.26	6.27	6.27
o-Dichlorobenzene	3.60	4.47	3.65	3.11	3.18	3.51	3.58	3.02	3.41	3.02	3.26	3.25	3.42

(6)

Hence, for low R_a high solubility and for high R_a low solubility is expected for each fullerene separately. Another important parameter for the numerical estimation of the degree of interaction between solute macromolecules and solvent molecules ("determination of miscibility") is the intermolecular parameter of Flory-Huggins χ , which provides simple predictions of the phase equilibrium for most solute-solvent mixtures ¹⁵

$$\chi_{1,2} = 0.34 + \frac{\nu_1}{RT} \left(\delta_1 - \delta_2 \right)$$

0.34 represents a correction factor for entropic contributions, v_1 is the molar volume of the solvent, δ_1 and δ_2 are the Hildebrand solubility parameter for the solvent and the solute, respectively. The determined intermolecular parameter of Flory-Huggins χ of

the selection of solvents are summarized in Table S12.

Solvents	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
Chlorobenzene	0.439	0.433	0.414	0.433	0.432	0.440	0.441	0.432	0.436	0.432	0.433	0.433	0.434
Chloroform	0.700	0.690	0.657	0.690	0.689	0.701	0.702	0.688	0.695	0.689	0.690	0.691	0.691
o-xyelene	0.734	0.721	0.679	0.721	0.720	0.736	0.739	0.719	0.727	0.719	0.720	0.722	0.723
Toluene	0.667	0.656	0.619	0.656	0.655	0.668	0.671	0.654	0.661	0.654	0.655	0.657	0.657
o-Dichlorobenzene	0.367	0.363	0.354	0.364	0.363	0.367	0.368	0.362	0.365	0.363	0.363	0.364	0.364

Table S12. Intermolecular parameter χ for ICBA-*e*, ICBA-*trans*-a, ICBA-*trans*-b and ICBA- *trans*-c in a selection of solvents.

The lower the intermolecular parameter χ , the higher the miscibility (good solubility) is expected. Now, the chemical potential μ_{mix} of the mixture of the fullerenes in the selected solvents are illustrated (Table S13):

Table S13. Chemical potential μ_{mix} in kJ/mol for ICBA-*trans*-a, ICBA-*trans*-b and ICBA-*trans*-c in a selection of solvents in a ratio of 0.998/0.002 of the mole fractions of the solvent/fullerene.

Solvents	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
Chlorobenzene	-78.12	-77.26	-67.19	-73.76	-75.30	-77.80	-78.18	-72.78	-77.22	-72.73	-76.04	-76.06	-76.05
Chloroform	-73.13	-72.30	-62.36	-68.92	-70.38	-72.83	-73.16	-67.94	-72.24	-67.90	-71.09	-71.10	-71.08
o-xyelene	-77.40	-76.54	-67.24	-73.21	-74.57	-77.04	-77.43	-72.33	-76.46	-72.27	-75.32	-75.31	-75.31
Toluene	-78.61	-77.74	-6.28	-74.35	-75.77	-78.26	-78.65	-73.45	-77.69	-73.40	-76.53	-76.54	-76.53
o-Dichlorobenzene	-76.78	-75.92	-65.86	-72.42	-73.95	-76.45	-76.83	-71.42	-75.86	-71.37	-75.72	-74.46	-74.69

The lower the chemical potential of mixtures μ_{mix} , the higher the solubility is expected. The solubility trends for these different methods are shown in Table S14, in which the numbers represent the better solubility by 1, the second better by 2, the third by 3, and the worse by 4.

Table S14. R_a , χ and μ_{mix} trends for ICBA-*trans*-a, ICBA-*trans*-b and ICBA-*trans*-c in a selection of solvents; 1 means the better solvent, 2 the second better..5 the worse

R _a	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
Chlorobenzene	1	1	1	2	1	1	1	2	1	2	1	1	1
Chloroform	5	5	4	5	5	5	5	5	5	5	5	5	5
o-xyelene	4	4	5	4	4	4	4	4	4	4	4	4	4
Toluene	3	3	3	3	3	3	3	3	3	3	3	3	3
o-Dichlorobenzene	2	2	2	1	2	2	2	1	2	1	2	2	2
X	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3c	4a	4b	4c
Chlorobenzene	2	2	2	2	2	2	2	2	2	2	2	2	2
Chloroform	4	4	4	4	4	4	4	4	4	4	4	4	4
o-xyelene	5	5	5	5	5	5	5	5	5	5	5	5	5
Toluene	3	3	3	3	3	3	3	3	3	3	3	3	3
o-Dichlorobenzene	1	2	1	1	1	1	1	1	1	1	1	1	1

μ_{mix}	<i>e</i> 1	е2	1a	1b	2a	2b	2c	3a	3b	3с	4a	4b	4c
Chlorobenzene	2	2	3	2	2	2	2	2	2	2	2	2	2
Chloroform	5	5	5	5	5	5	5	5	5	5	5	5	5
o-xyelene	3	3	2	3	3	3	3	3	3	3	3	3	3
Toluene	1	1	1	1	1	1	1	1	1	1	1	1	1
o-Dichlorobenzene	4	4	4	4	4	4	4	4	4	4	4	4	4

For the intermolecular parameter of Flory-Huggins (χ) we can compare also the fullerenes:

Table S15. Comparison of relative solubilities in for ICBA-*e*1 and ICBA-*e*2 fullerenes for the method χ in a selection of solvents; 1 means the fullerene that dissolves better in the solvent, 2 the second

X	ICBA-e1	ICBA-e2
Chlorobenzene	2	1
Chloroform	2	1
o-xyelene	2	1
Toluene	2	1
o-Dichlorobenzene	2	1

Table S16. Comparison of relative solubilities in for ICBA-*trans*-1a and ICBA-*trans*-1b fullerenes for the method χ in a selection of solvents; 1 means the fullerene that dissolves better in the solvent, 2 the second

X	ICBA-trans-1a	ICBA-trans-1b
Chlorobenzene	1	2
Chloroform	1	2
o-xyelene	1	2
Toluene	1	2
o-Dichlorobenzene	1	2

Table S17. Comparison of relative solubilities in for ICBA-*trans*-2a, ICBA-*trans*-2b and ICBA-*trans*-2c fullerenes for the method χ in a selection of solvents; 1 means the fullerene that dissolves better in the solvent, 2 the second better and 3 the worse

χ	ICBA-trans-2a	ICBA-trans-2b	ICBA-trans-2c
Chlorobenzene	1	2	3
Chloroform	1	2	3
o-xyelene	1	2	3
Toluene	1	2	3
o-Dichlorobenzene	1	2	3

Table S18. Comparison of relative solubilities in for ICBA-*trans*-3a, ICBA-*trans*-3b and ICBA-*trans*-3c fullerenes for the method χ in a selection of solvents; 1 means the fullerene that dissolves better in the solvent, 2 the second better and 3 the worse

X	ICBA-trans-3a	ICBA-trans-3b	ICBA-trans-3c
Chlorobenzene	1	3	2

Chloroform	1	3	2
o-xyelene	1	3	2
Toluene	1	3	2
o-Dichlorobenzene	1	3	2

Table S19. Comparison of relative solubilities in for ICBA-*trans*-4a, ICBA-*trans*-4b and ICBA-*trans*-4c fullerenes for the method χ in a selection of solvents; 1 means the fullerene that dissolves better in the solvent, 2 the second better and 3 the worse

X	ICBA-trans-4a	ICBA-trans-4b	ICBA-trans-4c
Chlorobenzene	1	2	3
Chloroform	1	2	3
o-xyelene	1	2	3
Toluene	1	2	3
o-Dichlorobenzene	1	2	3

The behavior of solid–liquid equilibria (SLE) is the most complex solubility cases than other phase equilibria as vapor–liquid equilibria (VLE) or liquid–liquid equilibria (LLE). Different types of SLE have to be distinguished. The type of SLE mainly depends on the mutual solubility of the components in the solid phase. There are systems with partial and total miscibility in the solid phase. The formation of solid solutions mainly depends on how well the lattice structure of solid compounds fits to the lattice structure of the liquid compounds. Thus, SLE depends of the compounds similarity in structures and sizes of the compounds. Thus, solid and liquid coexist in the two-phase region due to their thermal (same temperature) and mechanical equilibrium (equal pressure). From the fundamental thermodynamics it can be shown that the phase equilibrium condition is given by:

$$\mu_{solute}^{sol.}(\sigma) = \mu_{solvent}^{liq.}(\sigma)$$
(7)

In the case of mixing of solvents, the chemical potential of the mixture $\mu(\sigma)$ is equivalent to the Gibbs energy of the mixing

$$\Delta G_{mix} = \Delta H_{mix} - T \,\Delta S_{mix} \tag{8}$$

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. If ΔG_{mix} is negative, mixing is favorable. The entropy of mixing is generally calculated statistically for random mixture and can be very large for mixtures of small molecules. In which case, ΔH_{mix} can be relatively large without prohibiting the mixing. However, for solutions of macromolecules such as polymers in solvents, ΔS_{mix} is much smaller. This means that for mixing to occur, ΔH_{mix} must be below a critical value, which is relatively small. In this scenario, it is very important to understand what determines ΔH_{mix} for a given solute–solvent combination. Such understanding would allow solvents to be chosen to minimize ΔH_{mix} and so facilitate dissolution. Hildebrand and Hansen solubility parameters are based of this minimization of the enthalpy of mixing and for thou are commonly used to identify suitable solvents.

As the system is in equilibria state, it is useful to introduce the change of the Gibbs energy Δg as a function of the enthalpy (the Gibbs–Duhem equation):

$$\Delta G_{mix} = \Delta H_{m,i} - T\Delta S_{m,i} =$$

$$\Delta H_{m,i} - T \frac{\Delta H_{m,i}}{T_{m,i}} = RT \ln \left(\frac{X_i^T Y_i^T}{X_i^S Y_i^S} \right)$$

$$\ln \left(X_i^S Y_i^S \right) = - \frac{\Delta H_{m,i}}{RT} \left(1 - \frac{T}{T_{m,i}} \right)$$

(9)

where the enthalpy of fusion ($\Delta H_{m,i}$) the and the melting temperature ($T_{m,i}$) are necessary to be known.

$$\ln \left(V_{i}^{S} \right) = \frac{V_{1}}{RT} \varphi_{2}^{2} \left(\delta_{1} - \delta_{2} \right)^{9}$$

$$\Rightarrow \ln \left(V_{i}^{S} \right) = \frac{V_{solute}}{RT} \varphi_{solvent}^{2} \left(\delta_{1} - \delta_{2} \right)^{9}$$
(10)
(11)

where v_{solute} is the QSPRs–molar volume, *R* is the gas constant, and *T* is the absolute temperature. $\Phi_{solvent}$ is the volume fraction of the solute and is approximately the unity for sufficient dilute solutions:

$$\ln\left(X_{i}^{S}Y_{i}^{S}\right) = \frac{\mu_{mix}}{RT}$$
(12)

For the previous equations, we can derive:

$$-\ln\left(X_{i}^{S}\right) = \frac{V_{solute}}{RT} \varphi_{solvent}^{2} \left(\delta_{1} - \delta_{2}\right)^{2} + \frac{\mu_{mix}}{RT}$$
(13)

and then the mole fraction solubility belongs:

$$X_{i} = e^{-\frac{V_{1}}{RT}\varphi_{2}^{2}(\delta_{1}-\delta_{2})^{2}-\frac{\mu_{mix}}{RT}}$$
(14)

References

1 Y. Nakamura, K. O-kawa, M. Matsumoto, J. Nishimura, Tetrahedron 2000, 56, 5429.

2 J.H. Hildebrand, R.L. Scott, Solubility of Non-electrolytes, 3rd ed., Reinhold, New York, 1950.

3 Charles M. Hansen, J. Paint. Tech., 1967, 39

4 C.M. Hansen, A. Beerbower, Solubility parameters, in: *Kirk-Othmer Encyclopedia of Chemical Technology, Suppl. Vol. 2nd ed., Interscience, New York*, 1971, 889.

5 Adrien Benazzouz, Laurianne Moity, Christel Pierlot, Valerie Molinier, and Jean-Marie Aubry, *Colloids and Surfaces A: Physicochemical and Eng. Aspects* 2014, **458**.

6 Thomas Living, Michael L. Michelsen, Georgios M. Kontogeorgis, Fluid Phase Equilib- ria 2002, 203, 247.

7 HyperChem 7, Hypercube, Inc. Publication HC70-00-01-00 2002

8 TURBOMOLE: COSMOlogic GmbH and Co. KG, Imbacher Weg 46, 51379 Leverkusen, Germany (info@cosmologic.de)

9 A. Klamt, COSMO-RS: From quantum chemistry to fluid phase thermodynamics and drug design, *Elsevier Science Ltd., Amsterdam*, 2005.

10 G. Járvás, C. Quellet, A. Dallos, Fluid Phase Equilib. 2011, 309, 8.

11 J. D. Perea, S. Langner, M. Salvador, J. Kontos, G. Jarvas, F. Winkler, F. Machui, A. Gorling, A. Dallos, T. Ameri, C. J. Brabec, *J. Phys. Chem. B* 2016, **120**, 4431.

12 A. Klamt. J. Phys. Chem., 1995, 99, 2224.

13 A. Klamt, F. Eckert, W. Arlt, Annu. Rev. Chem. Biomol. Eng. 2010, 1, 101.

14 F. Machui, S. Langner, X. Zhu, S. Abbott, C. J. Brabec, Sol. Energy Mater. Sol. Cells 2012, 100, 138.

15 R. Colby, M. Rubinstein. Polymer Physics. New-York: Oxford University, 2003, 100, 274.