Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Non-Halogenated Solvents for Environmental Friendly Processing of High-Performance Bulk-Heterojunction Polymer Solar Cells

Chu-Chen Chueh,[a,b] Kai Yao,[a,c] Hin-Lap Yip,[a,#] Chih-Yu Chang,[a] Yun-Xiang Xu,[a] Kung-Shih Chen,[a] Chang-Zhi Li,[a] Peng Liu,[d] Fei Huang,[d] Yiwang Chen,[c] Wen-Chang Chen,[b] and Alex K.-Y. Jen*[a]

[a]Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195-2120, USA. E-mail: ajen@u.washington.edu

[b]Department of Chemical Engineering, and Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan

[c]Institute of Polymers/Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

[d]State Key Laboratory of Luminescence Physics and Chemistry, South China University of Technology, Guangzhou 510640, P. R. China.

[#]Current Address: State Key Laboratory of Luminescence Physics and Chemistry, South China University of Technology, Guangzhou 510640, P. R. China.

Device Fabrication and Characterization of FET: Field-effect transistors were fabricated through the top-contact and bottom-gate geometry. Heavily doped p-type silicon <100> substrates with a 300 nm thermal oxide layer were purchased from Montco Silicon Technologies INC. After cleaning the substrate by sequential ultrasonication in acetone and isopropyl alcohol for 15 min followed by air plasma treatment, the oxide layer was passivated with a thin divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) buffer layer. Polymer thin films were spin-coated from a 0.5 wt % solution. BHJ films were spin-coated from a solution of PDITT-DFBT:$PC_{71}BM$ blend (1:3).[1] Interdigitated source and drain electrodes (W=1000 μm, L= 20/50 μm) were defined by evaporating Au (40 nm) through a shadow mask under high vacuum ($< 2 \times 10^{-6}$ Torr). OFET characterization was carried out in a N_2–filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of $(I_{ds})_{1/2}$ *vs* V_{gs}. The threshold voltage (V_t) was estimated as the x intercept of the linear section of the plot of $(I_{ds})_{1/2}$ *vs* V_{gs}. The sub threshold swing was calculated by taking the inverse of the slope of I_{ds} *vs* V_{gs} in the region of exponential current increase.

***Device Fabrication and Characterization of OPV*:** ITO-coated (15 Ω/sq) glass substrates were cleaned sequentially with a detergent, DI-water, acetone, and isopropanol. Prior to the fabrication of the organic layers, the ITO surface was treated with UV-Ozone. For conventional structure, PEDOT:PSS (Baytron 4083) was first deposited on these ITO substrates (~ 40 nm) and then baked at 140 °C for 10 min. To avoid oxygen and moisture, the photoactive layers consisting of PIDTT-DFBT/PBDT-DTNT and $PC_{71}BM$ BHJ was spin-coated from the solutions of the studied solvents in an N_2-filled glovebox. After spin-coating the photoactive layers, all the samples were thermally annealed at 110 °C for 10 min. Fullerene surfactant layer was further spun onto the active layer and then thermally annealed at 110 °C for 5 min. Finally, Ag (100 nm) were thermally evaporated under high vacuum ($< 2 \times 10^{-6}$ Torr) to serve as cathode. For the PIDTT-DFBT:$PC_{71}BM$ BHJ inverted structures, the prepared sol-gel ZnO was spin-coated on the pre-cleaned ITO-coated glass substrate at 4000 rpm and then annealed at 200 °C for 1 h in the air. The C_{60}-SAM was further deposited on the ZnO surface using a two-step spin process.[2] Afterward, the same process used for active layer in the conventional structure devices was also applied for the inverted devices. Finally, 10 nm MoO_x and 100 nm Ag were sequentially thermally evaporated under high vacuum ($< 2 \times 10^{-6}$ Torr). As for the P3HT:$IC_{60}BA$ inverted devices, a ZnO precursor solution, consisting of 20 mg/ml zinc acetylacetonate hydrate in ethanol, was spin-coated onto ITO-coated glass, and then the C_{60}-SAM was deposited onto the ZnO surface as well.[2] The photoactive layers from the mixing solutions (17 mg/ml P3HT and 17mg/ml $IC_{60}BA$) of the studied solvents were then spin-coated without further solvent annealing. Subsequently, the PEDOT:PSS solution diluted with equal volume of isopropyl alcohol and 0.2 wt% of Zonyl FSO fluorosurfactant, was spin-coated on top of the active layer. Afterward, a top electrode of 150 nm Ag were thermally evaporated under high vacuum (< 2 x 10^{-6} Torr). Finally, the complete devices were thermally annealed at 150 ^{o}C for 7 mins. For all OPV devices, the active area was defined as 10.08×10^{-2} cm^2 by the designed shadow masks. All the *J-V* curves in this study were recorded using a Keithley 2400 source measure unit. The device photocurrent was measured under illumination from a 450 W Thermal Oriel solar simulator (AM 1.5G). The illumination intensity of the light source was accurately calibrated employing a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of National Renewable Energy Laboratory (NREL).[3] The calibration method, based on the IEC-69094-1 spectrum, followed procedures described previously.[3] The EQE spectra performed here are obtained by the IPCE measurement using the combination of a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, chopper with frequency of 100Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration. The absorption and transmission spectra were measuredusing a Perkin-Elmer Lambda-9 UV-visible spectrophotometer. Tapping-mode AFM images were taken on a Veeco multimode AFM with a Nanoscope III controller.

Table S1. Physical Properties of the Xylenes and Trimethylbenzenes.

	o-xylene	*m*-xylene	*p*-xylene	1,2,4-TMB	1,2,3-TMB	Mesitylene
Density (g/ml)[a]	0.88	0.86	0.86	0.88	0.89	0.86
Boiling Point (°C)[a]	144.50	139.12	138.37	169.38	176.12	164.74
Melting Point (°C)[a]	-25.20	-47.80	13.25	-43.77	-25.40	-44.72
Vapor Pressure (kPa at 25°C)[a]	0.88	1.13	1.19	0.30	0.20	0.33
Viscosity (mPa.s)[a]	0.760	0.581	0.603	1.11[d]	n/a	1.04[d]
Dielectric Constant (ε_r)[a]	2.56	2.36	2.27	2.38	2.66	2.28
Surface Tension (mN/m)[b]	29.76	28.47	28.01	29.20	n/a	27.55
Solubility of Fullerene (mg/ml)	8.7[c]	1.4[c]	5.9[c]	17.9[c]	n/a	1.70[c]

[a] "Laboratory Solvents and Other Liquid Reagents" in CRC Handbook of Chemistry and Physics, 90th Edition (Internet Version 2010), David R. Lide, ed., CRC Press/Taylor and Francis, Boca Raton, FL; [b] "Surface Tensions of Common Liquids" in CRC Handbook of Chemistry and Physics, 90th Edition (Internet Version 2010), David R. Lide, ed., CRC Press/Taylor and Francis, Boca Raton, FL; [c] From ref. [4]; [d] Materials Handbook, F. Cardarelli, Springer, London, 2000

Table S2. Physical Properties of Methylnaphthalene-based Solvent Additives

Processing Solvent	1-Methylnaphthalene (1-MN)	2-Methylnaphthalene (2-MN)	1,2-Dimethylnaphthalene (1,2-DMN)
Density (g/ml)	1.001	1.000	1.013
Boiling Point (°C)	240 ~ 243	241~242	266 ~ 267
Melting Point (°C)	-22	34 ~ 36	-2 ~ -1

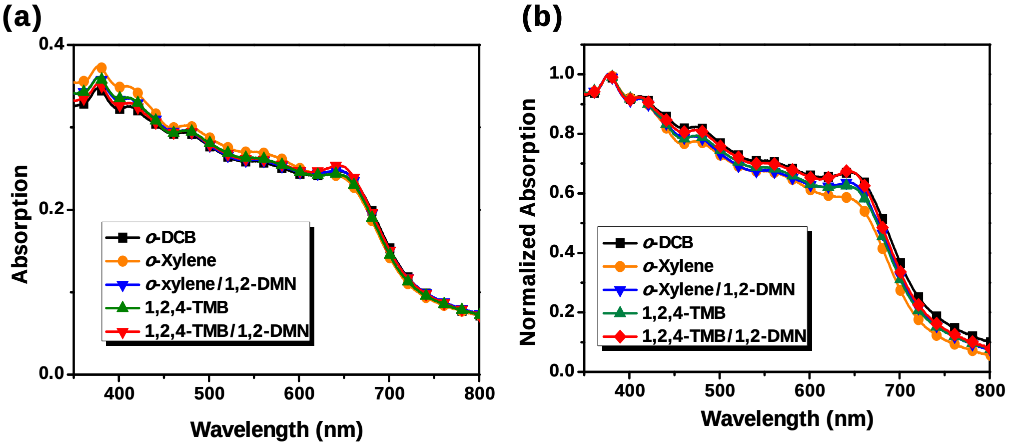

Figure S1. (a) Primary and (b) Normalized UV-vis spectra of PIDTT-DFBT:$PC_{71}BM$ BHJ processed from the studied solvents. The concentration of 1,2-DMN is 2.5% by volume.

Table S3. The summarized photovoltaic parameters of the studied solar cell devices processed from non-halogenated co-solvents.

	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE (%)
o-xylene	0.97	8.08	0.47	3.71
o-xylene/1-MN[a]	0.97	12.76	0.57	7.04
o-xylene/2-MN[a]	0.97	12.47	0.57	6.93
o-xylene/1,2-DMN[a]	0.97	12.89	0.57	7.15

[a] The concentration of 1-MN, 2-MN, and 1,2-DMN is 2.5% by volume.

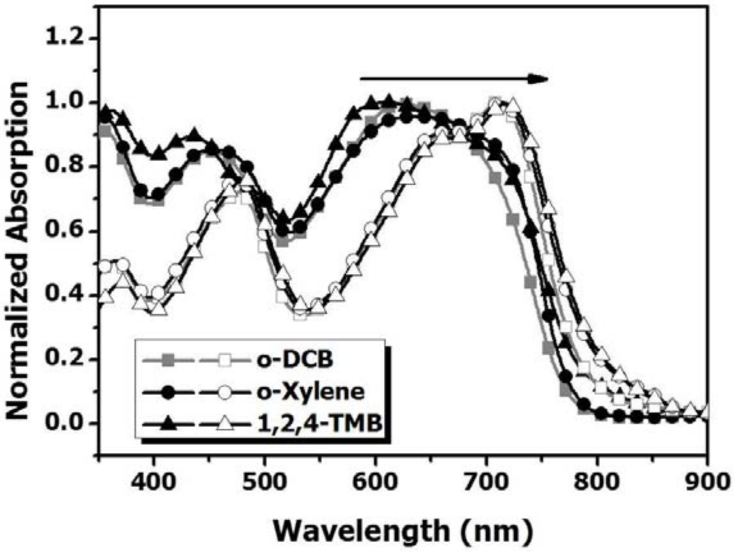

Figure S2. (Solid) Solution and (hollow) thin film states UV-vis spectra of PBDT-DTNT with different studied solvents.

Table S4. The summarized photovoltaic parameters of the P3HT:IC$_{60}$BA solar cell devices processed from non-halogenated solvents.

	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE (%)
o-DCB	0.84	9.79	0.56	4.60
o-xylene	0.80	6.62	0.43	2.27
1,2,4-TMB	0.83	6.27	0.42	2.20

References:

[1] Y. X. Xu, C. C. Chueh, H. L. Yip, F. Z. Ding, Y. X. Li, C. Z. Li, X. S. Li, W. C. Chen, A. K. Y. Jen, *Adv. Mater.*, 2012, **24**, 6356-6361.

[2] S. K. Hau, H. L. Yip, H. Ma, A. K. Y. Jen, *Appl. Phys. Lett.*, 2008, **93**, 233304.

[3] V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Adv. Funct. Mater.*, 2006, **16**, 2016-2023.

[4] R. S. Ruoff, D. S. Tse, R. Malhotra, D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379-3383.

Appendix

Health and Environmental Effects of Toluene:[1] Effects of toluene on human health and the environment depend on how much toluene is present and the length and frequency of exposure. Effects also depend on the health of a person or the condition of the environment when exposure occurs. Breathing large amounts of toluene for short periods of time adversely affects the human nervous system, the kidneys, the liver, and the heart. Effects range from unsteadiness and tingling in fingers and toes to unconsciousness and death. Direct, prolonged contact with toluene liquid or vapor irritates the skin and the eyes. These effects are not likely to occur at levels of toluene that are normally found in the environment. Human health effects associated with breathing or otherwise consuming smaller amounts of toluene over long periods of time are not known. Repeatedly breathing large amounts of toluene, such as when "sniffing" glue or paint, can cause permanent brain damage. As a result, humans can develop problems with speech, hearing, and vision. Humans can also experience loss of muscle control, loss of memory, and decreased mental ability. Exposure to toluene can also adversely affect the kidneys. Laboratory animal studies and, in some cases, human exposure studies show that repeat exposure to large amounts of toluene during pregnancy can adversely affect the developing fetus. Other studies show that repeat exposure to large amounts of toluene adversely affects the nervous system, the kidneys, and the liver of animals. Toluene by itself is not likely to cause environmental harm at levels normally found in the environment. Toluene can contribute to the formation of photochemical smog when it reacts with other volatile organic carbon substances in air.

Health and Environmental Effects of Xylenes:[2] Xylene is a liquid, and it can leak into soil, surface water (creeks, streams, rivers), or groundwater. Xylene can enter the environment when it is made, packaged, shipped, or used. Most xylene that is accidentally released evaporates into the air, although some is released into rivers or lakes. Xylene can also enter soil, water, or air in large amounts after an accidental spill or as a result of an environmental leak during storage or burial at a waste site. Since xylene evaporates easily, most xylene that gets into soil and water (if not trapped underground) is expected to go into the air where it is broken down by sunlight into other less harmful chemicals within a couple of days. For this reason, xylene is rarely found in high concentrations in topsoil or surface water (river, creeks) unless there has been a recent spill or continuing source of contamination. Any xylene that does not evaporate quickly from soil or water is broken down by small organisms. Only very small amounts are taken up by plants, fish, and birds. Xylene below the soil surface may travel down through the soil and enter underground water (groundwater). Xylene may remain in groundwater for several months before it is finally broken down by small organisms. If a large amount of xylene enters soil from an accidental spill, a hazardous waste site, or a landfill, it may travel through the soil and contaminate drinking water wells

Scientists have found that the three forms of xylene have very similar effects on health. No health effects have been noted at the background levels that people are exposed to on a daily basis. Short-term exposure of people to high levels of xylene can cause irritation of the skin, eyes, nose, and throat; difficulty in breathing; impaired function of the lungs; delayed response to a visual stimulus; impaired memory; stomach discomfort; and possible changes in the liver and kidneys. Both short- and long-term exposure to high concentrations of xylene can also cause a number of effects on the nervous system, such as headaches, lack of muscle coordination, dizziness, confusion, and changes in one's sense of balance. Some people exposed to very high levels of xylene for a short period of time have died. Most of the information on health effects in humans exposed for long periods of time is from studies of workers employed in industries that make or use xylene. Those workers were exposed to levels of xylene in air far greater than the levels normally encountered by the general population. Many of the effects seen after their exposure to xylene could have been caused by exposure to other chemicals that were in the air with xylene. Results of studies in animals indicate that large amounts of xylene can cause changes in the liver and harmful effects on the kidneys, lungs, heart, and nervous system. Short-term exposure to very high concentrations of xylene causes death in animals, as well as muscular spasms, incoordination, hearing loss, changes in behavior, changes in organ weights, and changes in enzyme activity. Animals that were exposed to xylene on their skin had irritation and inflammation of the skin. Long-term exposure of animals to low concentrations of xylene has not been well studied, but there is some information that long-term exposure of animals can cause harmful effects on the kidney (with oral exposure) or on the nervous system (with inhalation exposure). Information from animal studies is not adequate to determine whether or not xylene causes cancer in humans. Both the International Agency for Research on Cancer (IARC) and EPA have found that there is insufficient information to determine whether or not xylene is carcinogenic and consider xylene not classifiable as to its human carcinogenicity.

Health and Environmental Effects of 1,2,4-trimethylbenzene:[3] Effects of 1,2,4-trimethylbenzene on human health and the environment depend on how much TMB is present and the length and frequency of exposure. Effects also depend on the health of a person or the condition of the environment when exposure occurs. Breathing large amounts of 1,2,4-trimethylbenzene for short periods of time adversely affects the human nervous system. Effects range from headaches to fatigue and drowsiness. TMB vapor irritates the nose and the throat. Prolonged contact with liquid TMB irritates the skin. These effects are not likely to occur at levels of 1,2,4-trimethylbenzene that are normally found in the environment. Human health effects associated with breathing or otherwise consuming smaller amounts of 1,2,4-trimethylbenzene are not known. The petroleumindustry has conducted several studies on the C9 fraction in response to an EPA request for testing. These studies show that repeat exposure to this mixture of chemicals in air adversely affects the reproductive system and the developing fetus of animals. EPA believes that adverse effects associated with exposure to the C9 fraction are similar to those expected to occur as a result of exposure to individual chemicals, like 1,2,4-tri-methylbenzene, that make up this mixture. 1,2,4-Trimethylbenzene by itself is not likely to cause environmental harm at levels normally found in the environment. MB can contribute to the formation of photochemical smog when it reacts with other volatile organic carbon substance in air.

References:

[1] Database of United States Environmental Protection Agency (EPA).

http://www.epa.gov/chemfact/f_toluen.txt

[2] Database of Agency of Toxic Substances and Disease Registry (ATSDR).

http://www.atsdr.cdc.gov/toxprofiles/tp71-c1.pdf

[3] Database of United States Environmental Protection Agency (EPA).

http://www.epa.gov/chemfact/f_trimet.txt