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ARTICLE

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In this study, we explored a wide range of green solvents to process the semiconductor layer TIPS-PEN (6,13-bis(triisopropylsilylethynyl)pentacene), as well as to demonstrate potential generality, several p- and n-type organic semiconductors, for the fabrication of organic thin-film transistors (OTFTs). Our data demonstrate that several solvent options enable good semiconductor film-forming morphologies and for optimized TIPS-PEN TFTs mobilities of ~0.5-2 cm^2/Vs, thus surpassing those of toxic chlorinated options. Furthermore, we employed a green cellulose-cinnamate gate dielectric to fabricate TIPS-PEN OTFTs where both the semiconductor and the dielectric were processed using green solvents demonstrating the feasibility of a more sustainable OTFT technology.

Introduction

The interest in electronic devices based on solution-processed organic semiconductors (OSCs) remains high due to their potential use for inexpensive, mechanically flexible, lightweight, and portable alternative to traditional silicon electronic technology.[1] Despite remarkable achievements in terms of OSC-based device electrical performance, reliability and stability, far less efforts addressed the needs to overcome the use of hazardous halogenated/aromatic solvents for their realization.[2] The solvent choice for the OSC-based device fabrication process is crucial to achieve optimal performance since it affects the self-assembly/aggregation of the OSC in solution and during film formation, thus ultimately, the TFT channel film morphology and charge transport characteristics.[1,3] To date, halogen-containing and/or toxic aromatic solvents have been the most investigated processing option since, among these selections, it is typically possible to find one or more enabling the formation of optimal OSC films, owing to their ability to dissolve a wide range of molecular or polymeric architectures, adequate viscosity, vapor pressure, and boiling point. However, these solvents, such as chloroform, chlorobenzene, toluene and other aromatics, are highly toxic and thus banned in mass-production electronic FAB factories.[4-6]

Recent regulatory requirements in the European Union, North America and developed Asian countries have the ultimate goal of restricting or banning the use of chemicals that may be harmful to human health or the environment. For instance, the European REACH Regulation 1907/2006[7] envisages a mechanism which forces companies to apply for an authorization if they want to use or distribute chemicals (including solvents) identified as Substances of Very High Concern (SVHC). A restriction (or banning) may be also applied[7] on the manufacturing, placing on the market or use of SVHC. Thus, health and safety regulations have a major impact on solvent selection. Particularly, chlorinated hydrocarbons, aromatics, and dipolar aprotic solvents such as N-methyl-pyrrolidone, NMP, are considered hazardous[7] because of their well-known chronic toxicity effects. Therefore, it is essential to replace them with safer unconventional ones,[8] especially those deriving from waste production[8-10] or from biomasses.[8,11] This reflects also on avoiding expensive storage and/or disposal of waste materials, thus enhancing the sustainability of the overall process.

To address green processing of organic semiconductors for solar photovoltaic (OPV) module applications, several groups have reported interesting results by using non-halogenated solvents/additives (e.g. 2-methyl tetrahydrofuran; 2-Me-THF, cyclopentylmethyl ether; CPME). [12-31] However, note that in several cases the halogenated solvent was replaced by aromatic or dipolar aprotic alternatives, which remain of concern in terms of environmental/health issues.[14-18,22,23,30] Additionally, in most studies it was required to tailor the OSC chemical structure to make it processable in the proposed solvent. Interesting tools have also been developed to help the selection of solvent(s) for specific OSCs used, for instance, for photovoltaic applications.[32,33] However, very few studies investigated OSC processing with non-halogenated solvents for OTFTs, and they once again relied on a material design strategy.[34-36] Only very recently, Noh and coworkers[37] investigated mesitylene-acetophenone solvent mixtures with different compositions to fabricate OTFTs based on benchmark polymers (e.g. N2200)[38] with performance rivalling or exceeding those achieved with OTFTs processed from conventional o-dichlorobenzene.

Here we report for the first time on the very wide selection of green solvents to process 6,13-

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x bis(triisopropylsilylethynyl)pentacene (TIPS-PEN, Figure 1), i.e. one of the most widely studied molecular OSC for OTFT research.[39] Furthermore, to demonstrate that this approach is not limited only to TIPS-PEN, we also explored several other p- and n-type semiconductors. The ultimate goal is to provide evidence that a more sustainable solvent and materials combination is possible.

To realize green solvent-processable TFTs with high figure of merits, the organic semiconductor should form a favourable morphology upon the cast of the given solvent. Additionally, the solvents should afford enough solubility for the semiconductor material (> ~1 mg/mL),[40] possess suitable boiling point, and viscosity. Therefore, besides the greenness requirement, we have optimized solvent selection based on the above criteria, using a bottom-gate/top-contact device geometry (Figure 1c). Our results demonstrate that devices from several green solvents exhibit comparable/exceeding field-effect mobilities to those from conventional chlorobenzene, 1,2-dichlorobenzene, chloroform, *o*-xylene, and toluene processing. Furthermore, as a proof-of-concept, we employed a green solvent-processed combination of a semiconductors and a cellulose-cinnamate dielectric (Figure 1b) for the demonstration of a more sustainable OTFT technology.

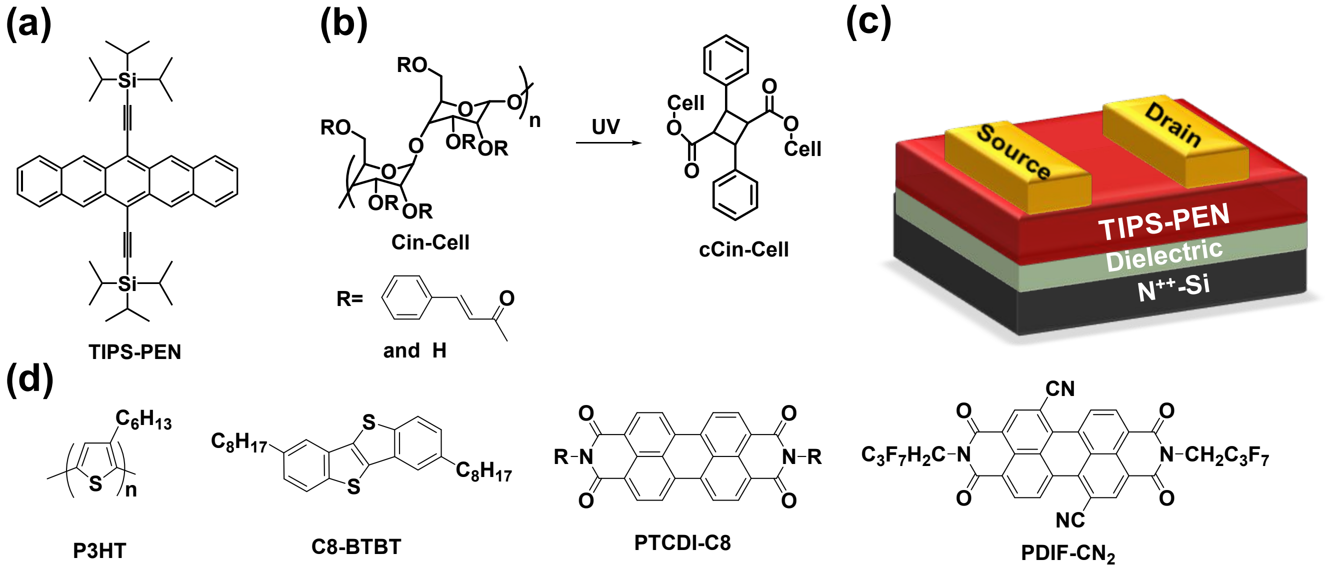

Figure 1. Chemical structure of (a) TIPS-PEN semiconductor; (b) cellulose cinnamate (Cin-Cell) dielectric precursor and the corresponding UV-promoted curing process to afford the cross-linked gate dielectric (cCin-Cell); (c) bottom-gate/top-contact (BG/TC) TFT geometry used for screening green solvents. (d) Chemical structure of additional p- and n-type semiconductors used in this study.

Experimental

Materials.

6,13-Bis(triisopropylsilylethynyl)pentacene, poly(3-hexylthiophene-2,5-diyl) (P3HT), 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT), N,N′-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8), N,N′-bis(n-alkyl)-(1,7 and 1,6)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDIF-CN2), and ω-hydroxy-polystyrene were purchased from Ossila Ltd., 1-Material Inc., SunaTech Inc., Tokyo Chemical Industry Co., Ltd., Flexterra, Inc., and Polymer source Inc., respectively. All semiconducting materials were used without further purification. The cellulose cinnamate polymer (Cin-Cell, Figure 1b) was synthesized according to the literature.[41]

Device fabrication

The OTFTs were fabricated by adopting the bottom-gate/top-contact (BG/TC) structure by using highly n-doped silicon wafers (resistivity < 0.005 Ω·cm) and a 300 nm thermally grown oxide layer (capacitance per unit area C_i = 11.4 nF/cm^2) as the gate contact/dielectric substrate. The substrates were cleaned *via* sonication in acetone for 10 min, followed by air plasma treatment for 5 min (Harrick plasma, PDC-32G, 18W). The TIPS-PEN, P3HT, C8-BTBT, PTCDI-C8, and PDIF-CN2 layers were coated *via* a solution-shearing (SS) method[42] on PS-brush-treated substrates. For the PS-brush treatment, PS-brush (M_w = 10–32 kgmol^{-1}) solutions were spin-coated on the cleaned substrates following a general procedure.[43] The Cin-Cell dielectric film (Figure 1b) was prepared according to the literature.[41] The concentration of the organic semiconductor solution, substrate temperature, and shearing speed were optimized for each type of solvent. After film formation, the substrates were placed in a vacuum oven at various temperatures and time periods to remove the residual solvent and develop proper crystallization (see table Table S1 for details). The OSC film thicknesses were measured by profilometer (DEKTAK-XT, Brucker) (Table S1). The device was completed by thermal evaporation of Au source and drain electrodes (40 nm) with various channel widths (W; 1000 and 500 μm) and lengths (L; 100 and 50 μm) through a shadow mask.

Characterization

The electrical performances of the OTFTs were characterized using a Keithley 4200 SCS under vacuum conditions. Carrier mobilities (μ) were measured in the saturation regime by the standard relationship, $\mu_{sat}=(2I_{DS}L)/[WC_i(V_G-V_T)^2]$, ($I_{DS}$; source-drain current, L; channel length, W; channel width, C_i; areal capacitance of the gate dielectric, V_G; gate voltage, V_T; threshold voltage). V_T was calculated by adapting the linear extrapolation method at the point of maximum $g_m(=dI_{DS}/dV_G)$.[44] The surface morphology and film microstructure of the thin films were measured by atomic force microscopy (AFM, NX10, Park Systems), and X-ray diffraction (XRD, Ultima IV, Rigaku), respectively.

Results and discussion

Thin-film transistor characterization

To investigate their applicability as a suitable medium for solution-processed OTFTs, several green solvents were tested by using TIPS-PEN as the organic semiconductor. The utilization of the semiconductor solution to fabricate thin-films was focused only on the solution shearing method in order to aim at producing highly ordered and anisotropic crystalline channel films.[45,46] Post-fabrication thermal annealing was utilized for additional film optimization in which the annealing temperature was selected based on the boiling point of the solvent.[47,48] Charge transport properties were accessed in a bottom-gate top-contact OTFT architecture (see experimental section for details). The electrical performances of all TIPS-PEN TFTs from different solvents are summarized in Table 1. Device performance from conventional aromatic or chlorinated solvents were also investigated for comparison. Thus, chlorobenzene, 1,2-dichlorobenzene, chloroform, *o*-xylene, and toluene-processed TIPS-PEN TFTs exhibited hole mobilities of 1.5, 0.66, 0.28, 1.3, and 0.39 cm^2 V^{-1}s^{-1}, respectively (Figures S1a-e). Bao et al. reported a state-of-the-art TIPS-PEN devices (toluene processed) using a solution shearing deposition technique with a maximum charge carrier mobility of 4.6 cm^2 V^{-1}s^{-1} (I_{on}/I_{off} ratio of ~10^7) using a different substrate and shearing conditions. Note, spin coated TIPS-PEN BG/TC OTFTs reported to date have typically shown field-effect mobilities 0.2 cm^2 V^{-1}s^{-1},[49] thus, our control devices exhibit performance in a reasonable range.

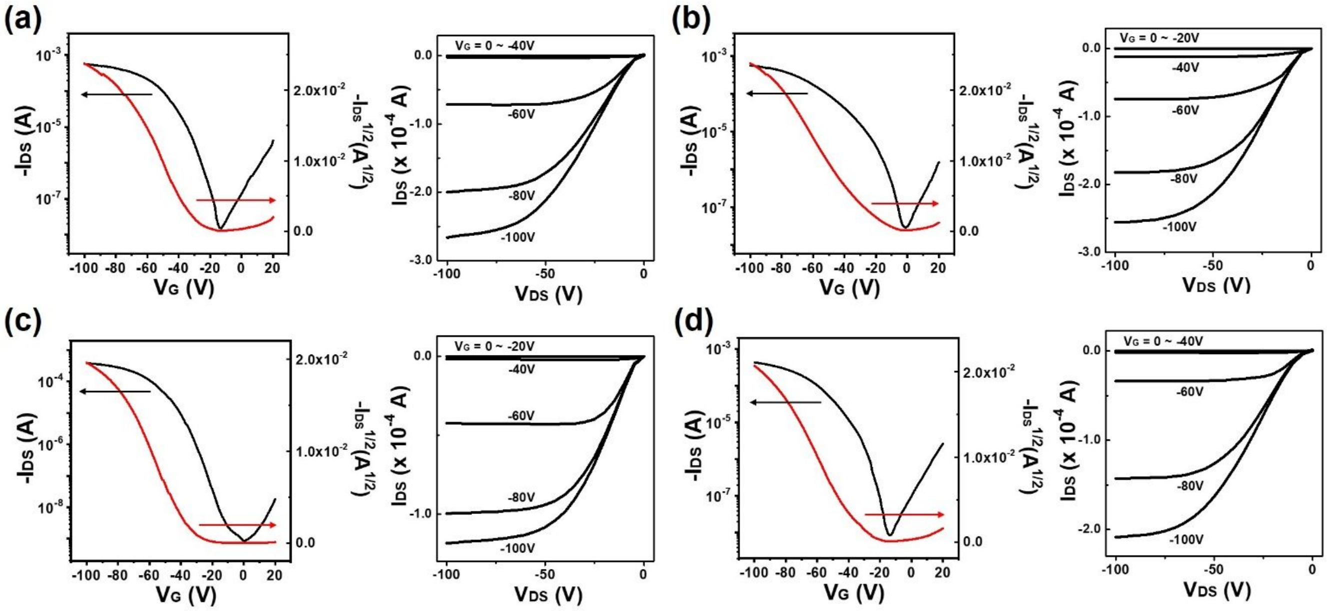

Figure 2. Transfer and output characteristics of TFT devices fabricated from (a) isobutyl acetate, (b) dimethyl carbonate, (c) anisole, and (d) t-amyl methyl ether. Channel width and length of 1000 μm and 50 μm, respectively, were employed for all of the devices.

Among the many different solvents in Table 1, devices fabricated from diethyl succinate, isobutyl acetate, isopropyl acetate, Purasolv EHL, dimethyl carbonate, anisole, t-amyl methyl ether, and Agnique AMD810 exhibit substantial hole mobilities of >1.0 cm^2 V^{-1}s^{-1} and current on-off ratios > ~10^5. Particularly, the isobutyl acetate devices exhibit an impressive μ of 2.6 with I_{on}:I_{off} > 10^4.

Clearly, these results demonstrate that green solvents could be competitor of conventional aromatic and/or chlorinated toxic solvents (Figures 2 and S1). These charge transport characteristics are consistent with the semiconductor film microstructure, as later described, due to formation of highly textured semiconductor films leading to efficient charge transport. Note that the I-V characteristic of several devices reveal the effect of the contact resistance at low voltages due contact-semiconductor energy level mismatch and bulk resistance through the semiconductor which dependents on the thickness and the morphology of the semiconductor film.[50,51] The latter is also reflected in large V_T values as seen in other top-contact devices.[52] The I-V hysteresis and subthreshold slopes (SS) of selected P5 devices were also analysed for the isobutyl acetate, dimethyl carbonate, anisole, and t-amyl methyl ether-processed devices, respectively (Figure S2). All devices exhibit exhibited lower back sweep current hysteresis accounting for 21, 27, 31, and 18 V, respectively, which is attributed to charge carrier trapping close to the channel or at the semiconductor/dielectric interface.[53] Consistently, the subthreshold slope (SS), which is closely related to the interface traps,[54] is found to be 4.7, 5.7, 6.5, and 4.7 V/decade, respectively. Note, we have not attempted here to optimize charge injection nor the quality of the dielectric surface functionalization, which could further optimize device performance when a proper solvent for the semiconductor is identified.

Furthermore, to demonstrate a more sustainable OTFT architecture, we have fabricated devices consisting of a solution-processed TIPS-PEN films from anisole and using as a gate dielectric a cellulose-cinnamate gate dielectric layer processed from the environmentally acceptable PGMA (propylene glycol methyl ether acetate) solvent (Figure S3a). These devices exhibit respectable performance with a hole mobility of 0.12 cm^2 V^{-1}s^{-1} and I_{on}:I_{off} > 10^4 (Figure S3b).

Finally, to generalize the use of the green solvents and provide evidence that they are not limited to TIPS-PEN, we initiated to investigate solution processing of several other organic semiconductors including p-type/polymeric poly(3-hexylthiophene-2,5-diyl) (P3HT), p-type/molecular 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) as well as n-type/molecular N,N′-dioctyl-3,4,9,10-perylenedi carboximide (PTCDI-C8) and N,N′-bis(n-alkyl)-(1,7 and 1,6)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDIF-CN2). As for TIPS-PEN, solution shearing was used for thin-film deposition. From the TFT results reported in the Electronic Supplementary Information (ESI, Figure S4 and Tables S2-S5), the initial data are promising though further performance enhancement could be achieved upon extensive optimization as for the TIPS-PEN devices. Thus, for the p-type semiconductors hole mobilities of ~0.01 cm^2 V^{-1}s^{-1} (P3HT) and ~ 1 cm^2 V^{-1}s^{-1} (C8-BTBT) can be achieved using cyclopentyl methyl ether and isopropyl acetate (or anisole), respectively. For the n-type transistors, the electron mobilities are ~ 0.1 cm^2 V^{-1}s^{-1} (PTCDI-C8) and ~ 0.07 cm^2 V^{-1}s^{-1} (PDIF-CN2) for semiconductor film processing in anisole and Purasolv EHL, respectively. Optimal I_{on}:I_{off} values vary for ~10^3 (P3HT and PDIF-CN2) to ~ 10^7 (PTCDI-C8) to > 10^8 (C8-BTBT). Therefore, these preliminary results demonstrate that decent device performance are achievable using green solvents.

TIPS-PEN thin-film morphology and microstructure

Since TIPS-PEN was investigated in detail, the semiconductor thin-film morphology and microstructure were accessed by atomic force microscopy (AFM) and θ-2θ x-ray diffraction (XRD) to corroborate the device characteristics. Atomic force microscopy (ESI, Figures S4c, S5, and S6) was employed to evaluate the solvent effect on the evolution of the TIPS-PEN thin film surface morphology and roughness. As depicted in Figures S4c and S5, micrometer-size crystalline morphologies with scattered small aggregates were observed for TIPS-PEN films processed from isobutyl acetate, dimethyl carbonate, anisole, and t-amyl methyl ether. Note that the relatively flat dark stripes arose along the shear stress of the solution shearing process, where the direction of the stripes corresponds with the shearing direction. Hence, the resulting films showed relatively large RMS surface roughness of 16 – 36 nm.

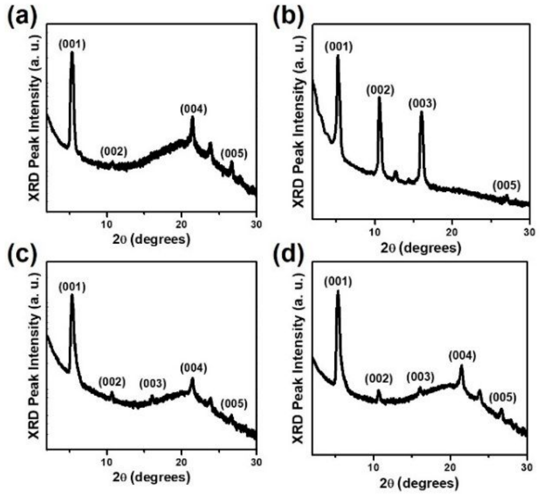

Figure 3. XRD scans for TIPS-PEN films from (a) isobutyl acetate, (b) dimethyl carbonate, (c) anisole, and (d) t-amyl methyl ether

Films from diethyl succinate, isopropyl acetate, Purasolv EHL, Agnique AMD810, chlorobenzene, 1,2-dichlorobenzene, chloroform, *o*-xylene, and toluene also exhibited similar morphologies (Figure S6). Furthermore, standard θ-2θ X-ray diffraction scans were performed to analyse microstructural order in the TIPS-PEN films (Figure 3 and ESI, Figures S4d and S7).

As depicted in Figure 3, isobutyl acetate, dimethyl carbonate, anisole, and t-amyl methyl ether-based thin films exhibited multiple reflections up to fifth-order, suggesting a highly crystalline microstructure of the corresponding thin films. The major primary diffraction peak (001) is observed at 2θ = 5.26 °, corresponding to a d-spacing of 16.8 Å, which is in good agreement to that of the previous results, denoting a well-ordered TIPS-PEN triclinic structure developing along the c-axis.[55]

Table 1. Summary of the TFT characteristics on Si/SiOx substrates of TIPS-PEN films processed from different solvents.

Solvent classification	**Solvent**	**T_s(°C)**	**μ_h(cm^{2}V^{-1}s^{-1})**	**V_t(V)**	**I_{ON}/I_{OFF}**
Alcohol	1,2-isopropylidene glycerol (Solketal)	140	no activity	-	-
	1-(2-hydroxyethyl)-2-pyrrolidone[a]	-	-	-	-
	1,3-propanediol[a]	-	-	-	-
Ester	2-ethylhexylacetate	140	no activity	-	-
	Diethyl succinate	140	1.0	-18	1.7×10^7
	Dimethyl adipate[a]	-	-	-	-
	Dimethyl succinate	140	0.00049	-31	1.1×10^4
	Esterol F	140	no activity	-	-
	Ethyl-4-oxopentanoate[a]	-	-		
	Ethylene glycol diacetate[a]	-	-	-	-
	Ethyl-L-lactate	80	0.01	-18	2.0×10^7
	γ-valerolactone	140	0.036	1.0	1.0×10^4
	Isobutyl acetate	70	2.6	-29	3.7×10^4
	Isopropyl acetate	50	0.67	-33	2.2×10^4
	IRIS	140	0.036	-9.3	1.9×10^2
	Isoamyl acetate	80	0.046	-44	5.2×10^4
	Loxanol	140	0.045	-27	6.6×10^5
	Methyl formate	20	0.00035	-28	1.8×10^5
	Methyl laurate	140	no activity	-	-
	Methyl oleate	140	no activity	-	-
	Methyl tetradecanoate	140	no activity	-	-
	n-amyl acetate	80	0.012	-29	2.9×10^5
	Pentyl-oxopentanoate	140	0.012	-19	1.7×10^6
	Purasolv EHL	140	1.8	-9.7	2.8×10^7
	Rapeseed oil methyl ester[a]	-	-	-	-
	Sec-butyl-4-oxopentanoate	140	no activity	-	-
	triacetin[a]	-	-	-	-
Carbonate	2-Methyl furfurylcarbonate[a]	-	-	-	-
	Diethyl carbonate	70	0.01	-33	4.0×10^5
	Dimethyl carbonate	70	1.3	-25	4.6×10^4
	Ethyl-(2-oxopyrrolidin-1-yl) methyl carbonate	140	no activity	-	-
	Methyl tetrahydrofurfuryl carbonate	140	no activity	-	-
	Propylene carbonate[a]	-	-	-	-
Ketone	Methyl ethyl ketone	45	0.013	-27	1.2×10^5
	cyclohexanone	90	no activity	-	-
Aromatic	p-cymene	110	0.00072	-47	1.2×10^5
	o-xylene	85	1.3	-46	3.1×10^5
	toluene	60	0.39	-40	1.3×10^6
Ether	1,3-dioxolane	40	no activity	-	-
	2-methyl THF	40	no activity	-	-
	Anisole	90	1.9	-33	4.4×10^5
	Cyclopentyl methyl ether	55	0.00080	-19	1.7×10^5
	Dimethoxymethane	20	0.000064	-39	7.3×10^3
	Plurafac LF711[a]	-	-	-	-
	Plurafac LF221[a]	-	-	-	-
	Plurafac LF303[a]	-	-	-	-
	Plurafac LF120[a]	-	-	-	-
	Dehypon LS54[a]	-	-	-	-
	Synperonic LF30[a]	-	-	-	-
	t-amyl methyl ether	50	1.4	-32	5.1×10^4
Dipolar aprotic	Polarclean	140	0.01	-16	1.2×10^8
	Steposol (N,N-dimethyl-9-decenamide)	140	no activity	-	-
	Agnique AMD810	140	1.3	-13	1.0×10^8
Chlorinated	Chlorobenzene	60	1.5	-45	1.4×10^6
	1,2-dichlorobenzene	140	0.66	-13	6.8×10^6
	Chloroform	25	0.28	-25	3.1×10^4

Ts = substrate temperature; [a]These solvents could not form films large enough to fabricate OTFT devices.

Table 2. Ranking of solvents investigated in this study for TIPS-PEN film processing.[a]

Classification	Solvent	Overall Green Assess.	B.p. (°C)	Viscosity	TIPS-PEN FFa	TIPS-PEN μ_h	Default Rank	Ranking after discussion
Alcohol	Solketal	🟨	🟩 188-189	🟨	🟩	🟥	🟥	🟥
	HEPyr	🟨	🟥 140-142[b]	🟥	🟥	🟥	🟥	🟥
	1,3-propanediol	🟨	🟩 214	🟥	🟥	🟥	🟥	🟥
Ester	2-ethylhexylacetate	🟩	🟩 199-200	🟩	🟩	🟥	🟥	🟨
	Diethyl succinate	🟨	🟩 216-218	🟩	🟩	🟩	🟩	🟨
	Dimethyl adipate	🟨	🟩 109-110	🟩	🟥	🟥	🟥	🟥
	Dimethyl succinate	🟩	🟩 200	🟩	🟩	🟥	🟥	🟨
	Esterol F	🟨	🟥 > 300	🟩	🟩	🟥	🟥	🟥
	Ethyl-4-oxopentanoate	🟨	🟩 220	🟩	🟩	🟥	🟥	🟥
	Ethylene glycolediacetate	🟩	🟩 186-187	🟩	🟥	🟥	🟥	🟨
	Ethyl-L-lactate	🟨	🟩 154	🟩	🟩	🟨	🟨	🟨
	γ-valerolactone	🟨	🟩 207-208	🟩	🟩	🟨	🟨	🟨
	🏅 i-butylacetate	🟩	🟩 116-117	🟩	🟩	🟩	🟩	🟩
	🏅 i-propylacetate	🟩	🟩 88.8	🟩	🟩	🟩	🟩	🟩
	IRIS	🟨	🟩 215.6	🟩	🟩	🟨	🟨	🟨
	Isoamyl acetate	🟩	🟩 142	🟩	🟩	🟨	🟨	🟩
	Loxanol	🟨	🟥 > 300	🟥	🟩	🟨	🟨	🟨
	Methyl formate	🟥	🟥 31-33	🟩	🟥	🟥	🟥	🟥
	Methyl laurate	🟨	🟨 261-262	🟩	🟩	🟥	🟥	🟥
	Methyl oleate	🟩	🟥 > 300	🟨	🟩	🟥	🟥	🟨
	Methyl tetradecanoate	🟨	🟥 323	🟩	🟩	🟥	🟥	🟥
	n-amyl acetate	🟩	🟩 149	🟩	🟩	🟨	🟨	🟩
	Pentyl-oxopentanoate	n.a.[c]	🟥 > 300	🟩	🟩	🟨	🟨	🟨
	Purasolv EHL	🟨	🟩 246	🟩	🟩	🟩	🟩	🟨
	Rapeseed oil methyl ester	🟩	🟥 > 300	🟥	🟨	🟥	🟥	🟨
	Sec-butyl-4-oxopentanoate	n.a.[c]	🟩 225-226	🟩	🟩	🟥	🟥	🟥
	triacetin	🟩	🟩 258	🟥	🟥	🟥	🟥	🟨
Carbonate	2-Methyl furfuryl carbonate	n.a.[c]	🟩 174	🟩	🟨	🟥	🟥	🟥
	Diethyl carbonate	🟩	🟩 126-128	🟩	🟩	🟨	🟨	🟩
	🏅 Dimethyl carbonate	🟩	🟩 90	🟩	🟩	🟩	🟩	🟩
	EPyrMC	n.a.[c]	🟥 > 300	🟨	🟩	🟥	🟥	🟥
	MTHFC	n.a.[c]	🟩 203	🟩	🟨	🟥	🟥	🟥
	Propylene carbonate	🟩	🟩 240-243	🟩	🟥	🟥	🟥	🟨
Ketone	Methyl ethyl ketone	🟨	🟩 80	🟩	🟩	🟨	🟨	🟨
	cyclohexanone	🟨	🟩 155	🟩	🟩	🟥	🟥	🟥
Aromatic	p-cymene	🟨	🟩 176-178	🟩	🟩	🟥	🟥	🟥
	o-xylene	🟨	🟩 144	🟩	🟩	🟩	🟩	🟨
	Toluene	🟨	🟩 110	🟩	🟩	🟩	🟩	🟨
Ether	1,3-dioxolane	🟨	🟩 74-75	🟨	🟩	🟥	🟥	🟥
	2-methyl THF	🟨	🟩 78-80	🟩	🟩	🟥	🟥	🟥
	🏅 Anisole	🟩	🟩 154	🟩	🟩	🟩	🟩	🟩
	Cyclopentyl methyl ether	🟨	🟩 106	🟩	🟩	🟥	🟥	🟥
	Dimethoxymethane	🟥	🟥 41-42	🟩	🟩	🟥	🟥	🟥
	Plurafac LF711	🟨	🟥 >300	🟥	🟥	🟥	🟥	🟥
	Plurafac LF221	🟨	🟥 >300	🟥	🟥	🟥	🟥	🟥
	Plurafac LF303	🟨	🟩 245-255	🟥	🟥	🟥	🟥	🟥
	Plurafac LF120	🟨	🟥 >300	🟥	🟥	🟥	🟥	🟥
	Dehypon LS54	🟨	🟥 >300	🟥	🟥	🟥	🟥	🟥
	Synperonic LF30	🟨	🟥 >300	🟥	🟥	🟥	🟥	🟥
	🏅 t-amyl methyl ether	🟩	🟩 85-86	🟩	🟩	🟩	🟩	🟩
Dipolar aprotic	Polarclean	🟨	🟨 280	🟨	🟩	🟨	🟨	🟨
	Steposol	🟨	🟨 297-298	🟩	🟩	🟥	🟥	🟥
	Agnique AMD810	🟨	🟨 274	🟩	🟩	🟩	🟩	🟨
Chlorinated	Chlorobenzene	🟨	🟩 132	🟩	🟩	🟩	🟩	🟥
	1,2-Dichlorobenzene	🟨	🟩 180	🟩	🟩	🟩	🟩	🟥
	Chloroform	🟥	🟩 61	🟩	🟩	🟩	🟩	🟥

[a] The green, yellow, and red colour codes represent preferred, problematic, and not recommended solvents, respectively. Abbreviations: FFa (Film Forming ability); HEPyr (1-(2-HydroxyEthyl)-2-Pyrrolidone); EPyrMC (Ethyl-(2-oxoPyrrolidin-1-yl) Methyl Carbonate); MTHFC (Methyl TetraHydroFurfuryl Carbonate); 🏅: "Fully green" criteria; [b] at 4 mbar; [c]SDS not available

Ranking of green solvents

To provide the community with insights on how to evaluate the greenness of certain solvents, Table 2 aims to compare the solvents' desirability both in a single chemical class (i.e. alcohols, esters, carbonates, ketones, aromatics, ethers, dipolar aprotics) and across multiple classes. Chlorobenzene, 1,2-dichlorobenzene, chloroform, *o*-xylene, and toluene are also included as reference entry. To this end, a classical colour code (green, yellow, red) has been used for each general area of assessment (i.e. solvent greenness, boiling point requirement for safety/processing, viscosity for thin-film/TFT processing; *vide infra* for discussion). These codes are also combined in a composite colour incorporating all these requirements, to give a ranking by default and “ranking after discussion” of each solvent (*vide infra*). Note, certain codes apply specifically to TIPS-PEN but this notation is extendable to other semiconductors. The solvent colour coding is inspired by the GlaxoSmithKline, GSK, and CHEM 21 solvent selection guides for the pharmaceutical industry.[4-6] These guides account for the physical and (eco)toxicity properties of solvents by transforming them into a scale to determine their greenness.

Particularly, the *preferred* solvents, i.e. solvents presenting a few issues, are displayed with the green colour code; the yellow colour code has been used for *problematic* solvents, i.e. solvents that can be used but their implementation may present issues or uncertainties; *not recommended* solvents are identified with red colour code, i.e. the constraints on the solvent use are very high. Thus, the colour codes associated to the overall greenness of the solvents in Table 2 are those from the existing benchmark guides,[4-6] when available. For solvents not yet included in the above guides the interactive spreadsheet made available by CHEM 21 consortium[5a] has been used to estimate the colour codes by employing the information extracted from the safety data sheets (SDS), provided their availability (see ESI).

In terms of safety as well as health and environmental hazards, the 51 solvents considered in this study generally perform well, except for methyl formate and dimethoxymethane. Moreover, it has to be highlighted that in the case of green solvents pentyl-4-oxopentanoate, sec-butyl-4-oxopentanoate, 2-methylfurfuryl carbonate, ethyl-(2-oxopyrrolydin-1-yl) methyl carbonate, and methyl tetrahydrofurfuryl carbonate, they do not possess sufficient data for their hazards classification (e.g. UN GHS Hazard Statements[56] are missing). For solvents where data gaps occur, the reader is advised that manifold approximations imply a lower level of confidence.

Boiling points are included in the overall greenness assessment based on industry guides.[4-6] However, a separate column was included in Table 2 listing the solvent b.ps, to take specifically into account their suitability for device processing. The associated colour codes are based on the ranges defined in Table 3. Extremely low boiling point solvents (T≤ 50°C) may not be suitable for solution processing and cannot be used in common FAB environments for safety concerns.[48] Table 3 also reports the value ranges for the solvent viscosity (η, mPa·s) coding, reflecting again the general solvent appropriateness for OTFTs processing. A film-forming ability scoring system has been also established (Tables 4 and 5). It combines assessments for both TIPS-PEN solubility as well as dewetting of the corresponding formulation since they have prime importance on the morphological quality of the resulting films.

Table 3. Ranking of boiling points (b.p., °C) and viscosity (η, mPa·s) values

Green	50<b.p. ≤260	$\eta \leq 5.0$
Yellow	260<b.p. <300	$5.0 < \eta \leq 15$
Red	b.p. ≥ 300 or b.p. ≤50	$\eta > 15$

Table 4. TIPS-PEN solubility and thin-film dewetting criteria

	Solubility (mg/mL)			dewetting	
	s ≥ 2	1 ≤ s< 2	s < 1	n	y
score	1	2	3	0	1

Table 5. Ranking of film-forming ability by score combination

Red	solubility score = 3
Red	two “red” score
Yellow	dewetting score= 1
Green	other

Finally, for the charge carrier mobility (μ, cm^{2}V^{-1}s^{-1}) we categorized them following the value ranges presented in Table 6. Thus, the ranking “by default” colour code is dominated by the TIPS-PEN OTFT charge carrier mobility criterion (Table 2).

Table 6. Ranking of charge carrier mobility values (cm^{2}V^{-1}s^{-1})

Green	$\mu > 0.1$
Yellow	$0.01 \leq \mu \leq 0.1$
Red	$\mu < 0.01$

Next, a ranking “after discussion” was assessed (Table 2, last column), as the result of an overall evaluation of the solvent greenness, thin-film forming, device characteristics, and potentiality for further improvement upon using different thin-film processing techniques or TFT architectures. Although Table 2 refers specifically to TIPS-PEN, some of the discussion and rationale are extendable, and more importantly is a useful resource, to initiate the screening and optimization for processing other semiconductors.

First, in the ranking “after discussion”, all chlorinated solvents are classified as “not recommended” despite the mobility value generates a “green” colour code. This is because of safety concerns and they are all banned in FAB lines. As a rule, we decided not to modify the ranking by default for “problematic” solvents (“yellow” code) leading to a TIPS-PEN OTFT μ_h lower than 0.01 cm^{2}V^{-1}s^{-1} (“red” code). Moreover, we confirmed the ranking by default for solvents for which the overall greenness assessment is not possible, i.e. SDS is currently non-existent, (pentyl-oxopentanoate, sec-butyl-4-oxopentanoate, 2-methyl furfuryl carbonate, ethyl-(2-oxopyrrolidin-1-yl) methyl carbonate, methyl tetrahydrofurfuryl carbonate) as well as for those having a clear ranking in the screening. Furthermore, we ranked as “recommended” isoamyl acetate, n-amyl acetate, and diethyl carbonate, though they provide TIPS-PEN TFT mobility values which are categorised as “yellow”. In fact, the promising device performance achieved here when using share printing/Si-SiO_x suggests that further improvements are worth pursuing using alternative thin-film processing approaches and/or TFT material combination/architectures. Similarly, because of the green credentials, 2-ethyl hexyl acetate, dimethyl succinate, ethylene glycolediacetate, methyl oleate, rapeseed oil methyl ester, triacetin and propylene carbonate where classified with a yellow code “after discussion”. Last, solvents which may present issues (“yellow” code) in terms of greenness, but affording mobilities > 0.1 $cm^2V^{-1}s^{-1}$ (e.g., o-xylene and toluene) are also ranked yellow, meaning that despite the good-to-excellent device performance, the community should consider alternatives.

From the overall evaluation, Table 2 highlights that optimal results in terms of combination of solvent greenness and TIPS-PEN device response are achieved when employing i-butyl acetate, i-propyl acetate, dimethyl carbonate, anisole, and t-amyl methyl ether, as pointed out by the green colour code associated with all the criteria under examination (“fully green” criteria). Notably, when using these solvents, TIPS-PEN device performances are similar to, or surpassing those, of reference devices. Importantly, some of the green solvents identified here (i-propyl acetate, dimethyl carbonate, anisole) also enable good performance for other semiconductors (ESI, Tables S2-S5), which further thin-film morphology/performance optimization is in progress.

Conclusions

In summary, we demonstrated the use of several green solvents for processing organic semiconductor films. TFTs fabricated with the benchmark organic semiconductor TIPS-PEN processed with these solvents exhibit mobilities which rival or exceed those obtained from conventional toxic/chlorinated solvents. Thus, a hole mobility > 1.0 $cm^2V^{-1}s^{-1}$ was obtained for several solvents such as diethyl succinate, isobutyl acetate, dimethyl carbonate, and t-amyl methyl ether. Particularly, the TIPS PEN devices processed from isobutyl acetate exhibit a remarkable μ up to 2.6 $cm^2V^{-1}s^{-1}$ with a I_{on}:I_{off} > 10^4. Other p- and n-type semiconductors can also achieve decent device characteristics, which could certainly be improved with further efforts. Furthermore, we also proved the concept of a more sustainable OTFT structure by employing green solvent-processed TIPS-PEN with a green solvent processed cellulose cinnamate gate dielectric material. We believe that this study can help the community to guide the optimization of organic electronic devices abiding by safety regulations and a more sustainable approach for materials processing.

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Conflicts of interest

There are no conflicts to declare.

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