

New triindole-based organic semiconductors: structure-property relationships

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ABSTRACT

We introduce a new family of stable high-mobility organic π -type semiconductors based on the electron-rich 10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole (triindole) extended π -conjugated system. This platform tends to form columnar stacks of the aromatic cores maximizing π -orbital overlap between adjacent molecules, thus paving the way for the one-dimensional migration of charge carriers along the columns. In addition these compounds have two different types of positions that can be functionalized independently offering the possibility of tuning their electronic properties as well as their morphology through chemical functionalization. The integration of the optimized triindole derivatives into solution processed devices as active layer is explored in this work.

Keywords: organic semiconductors, hole mobility, discotics

1. INTRODUCTION

The field of organic electronics evolves rapidly¹⁻³ moving in only a few years from a basic research level to the development of new generation devices already commercially viable. Although organic electronics are not intended to compete with their inorganic counterparts they are expected to exert a tremendous impact in the future semiconductor industry by low-cost, high diversity and low power consumption. However before these devices enter massively in the market several fundamental and technological challenges have to be faced, such as performance, stability, large area processing or even understanding the different factors affecting mobility in organic semiconductors.

Organic semiconductors with mobilities able to compete with amorphous silicon have already been developed, however these molecules have in many cases stability and processability problems. At this stage there is a significant need for new organic semiconducting materials that combine the ability to perform efficient charge transport with good processability and stability. In this context we became interested on a the electron-rich 10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole (triindole) a new organic semiconductor. The presence of delocalized π -electrons provides this platform interesting electronic properties, while its discotic topology induces highly ordered organizations due to stacking paving the way for a favorable overlap of π -orbitals and consequently to an increased charge mobility.

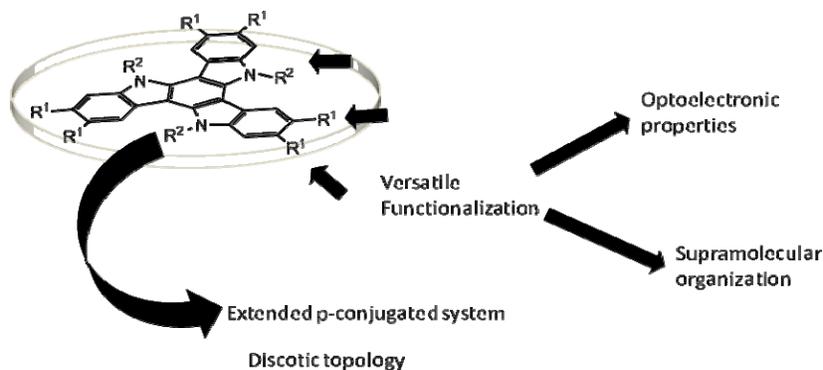


Fig.1. Characteristics of triindoles

In addition the platform of triindole presents two different types of positions that can be functionalized independently. The three *N*-positions can be easily functionalized taking advantage of the typical reactivity of azoles, while starting from known hexabromine triindol, the exploitation of cross-coupling methodologies opens flexible strategies to various peripheral functionalizations (Figure 1). The electronic communication of the external functional groups with the central electron-rich triindole core facilitate the tuning of the HOMO-LUMO levels of these molecules, while the adequate selection of the substituents allows us to influence in the final morphology of the material.

In this work, we explore the possibility of integration of active layers based on the presented materials in organic electronic devices by means of the fabrication and characterization of organic emitting diodes.

2. RESULTS AND DISCUSSION

2.1. Electronic properties of the platform

Organic single crystals offer an excellent opportunity to investigate structure-properties relationships and to elucidate charge transport mechanism in organic materials. Here, the properties are not masked by grain-boundaries or other microstructure features that can severely localize and trap the charge carriers. We have made an initial evaluation the semiconducting properties of this platform on the trimethylated derivative **1**. This molecule crystallizes forming a highly ordered columnar structure in which stacked molecules are situated at two alternating distances (3.53 Å and 3.68 Å) along the column as determined by single crystal X-ray diffraction analysis. These short intermolecular distances between adjacent units, make this system an ideal candidate for charge-transport processes along the stacks.

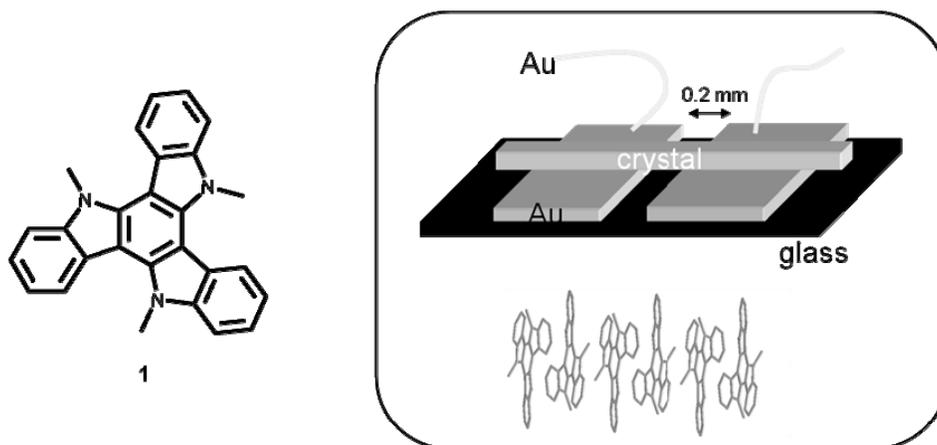


Fig. 2. Chemical structure of the *N*-trimethyltriindole **1** and schematic view of a device based on single crystals of this molecule

The electronic properties of this material have been studied both theoretically and experimentally. Its HOMO value is found to coincide with Au work function (5.1 eV), thus low barriers are expected for hole injection from gold electrodes. The hole-mobility of this material has been predicted theoretically considering a hopping-type mechanism for the charge transport and determined experimentally at the space-charge limited current (SCLC) regime of the current-voltage measurements. Both theoretical ($\mu_{\min} = 0.22 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and experimental ($\mu_{\min} = 0.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) values are in good agreement.⁴

While organic single crystals, largely free of grain boundaries or molecular disorder are the highest charge carrier mobility semiconductors, their fragility and brittleness make them very difficult to work with. In the search device-oriented molecular charge transport materials in addition to favorable electronic properties it is fundamental the morphology of the final material that will determine its processability morphology of the material. This will be crucial

for their performance and processability. The chemical versatility of this platform offers varied possibilities to fine tuning its electronic and morphologic properties in an independent way.

2.2. Structure-electronic properties relationships

The peripheral functionalization can be achieved starting from known hexabromine triindol taking advantage of the different cross-coupling catalyzed by transition metals. Thus six-fold Sonogashira coupling of **2** with arylalkynes substituted in the para position with functional groups with different electronic nature gave rise to a series of *p*-phenylethynylalkynes.⁵ Similarly Suzuki coupling of **2** with different Suzuki boronic acids yielded a family of star-shaped phenyl triindoles (Figure 3).⁶

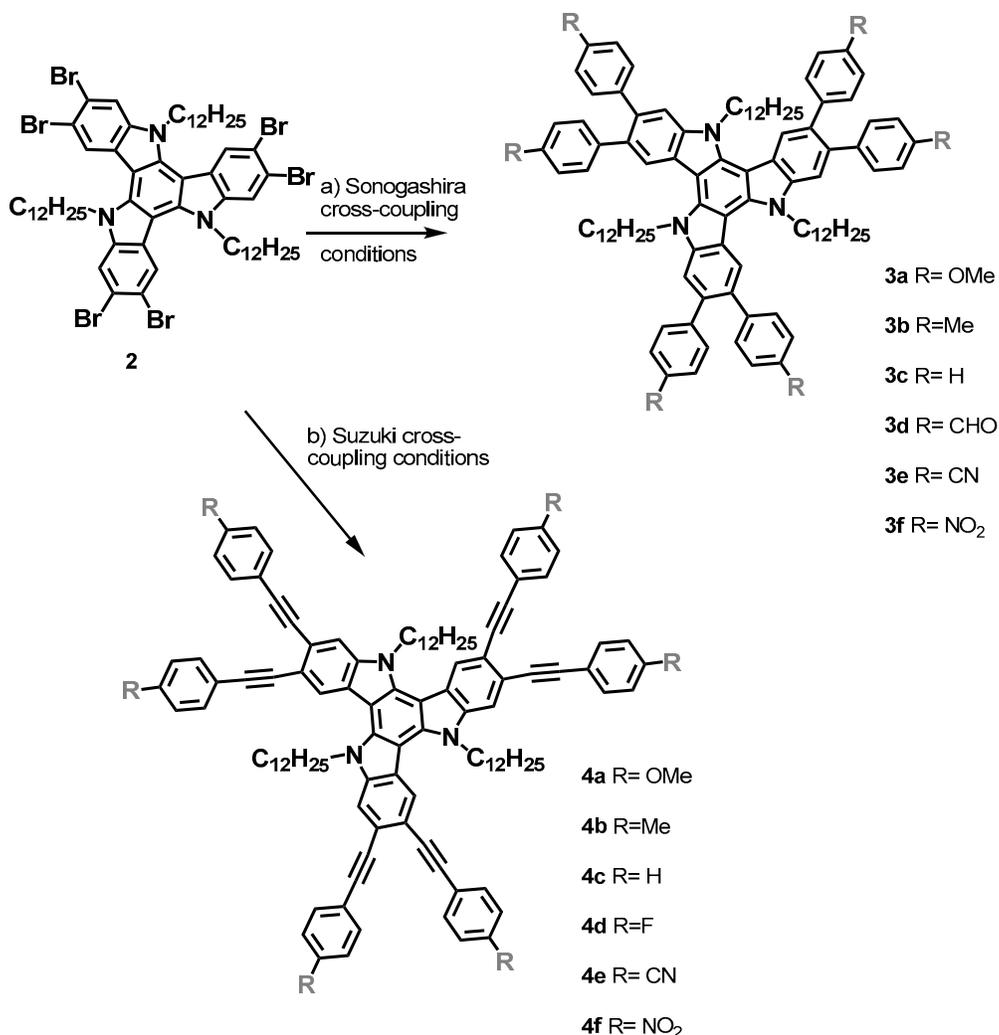


Fig. 3. Peripheral functionalization of triindoles

The influence of the six peripheral groups, in the electronic properties of these two families has been studied by cyclic voltammetry. The oxidizability of these molecules, associated to the easy generation of a cation radical in the electron-rich central platform,⁷ varies in agreement with the nature of the peripheral substituents. Thus, attaching electron-donating groups results in an increase of the electron density in the π system and in consequence in a shift of the oxidation potentials to lower values. In contrast, upon attaching peripheral electron withdrawing groups the oxidation

potentials shifts anodically as increasing the acceptor character of the substituents (Figure 4, see cyclic voltammograms of **3c** and **3e**).

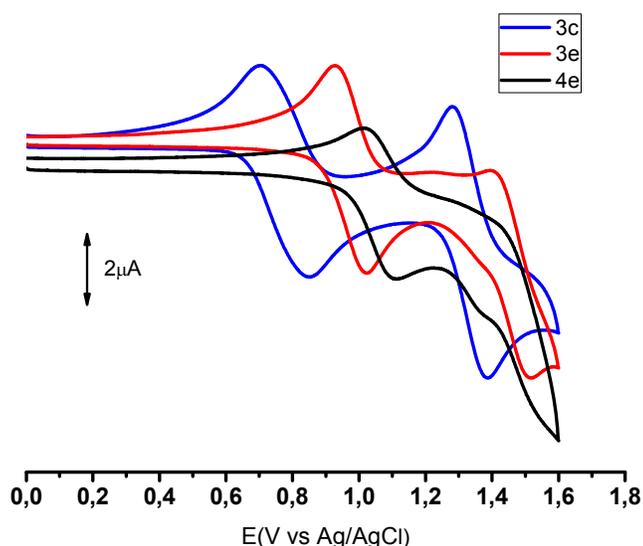


Fig. 4. Cyclic voltammogram of **3c**, **3e** and **4e** at $c=10^{-3}$ in CH_2Cl_2 and 0.1 M tetra-n-butylammonium-hexafluorophosphate (TBAPF₆) at a scan rate of 100mV/s using a Pt working electrode.

A clear influence of the extension of the π -conjugated system can be observed when we compare for example two derivatives substituted with equal peripheral groups but connected to the core by means of phenyl or phenylethynyl linker (Figure 4, see cyclic voltammograms of **3e** and **4e**). It can be observed how upon increasing the conjugation the system tends to lose its electrochemical reversibility with concomitant shift of the oxidation potential to higher values.

The HOMO energy value for these derivatives has been estimated from the first oxidation potential with respect to ferrocene, based on the value of -4.8 eV for Fc with respect to zero vacuum level. This value is obtained from the calculated value of -4.6 eV for the standard electrode potential (E°) using a normal hydrogen electrode (NHE) on the zero vacuum level and that of 0.2 V for Fc vs. NHE.⁸

Table 1. Values of HOMO-LUMO levels and optical HOMO-LUMO gap of hexaaryl **3** and hexaalkynyltriindoles **4**.

R	Hexaaryltriindoles			Hexaalkynyltriindoles			
	HOMO [eV]	LUMO [eV]	E_g^{opt} [eV] ^[a]	HOMO [eV]	LUMO [eV]	E_g^{opt} [eV] ^[a]	
3a	-5.07	-1.96	3.11	4a	-5.12	-2.20	2.92
3b	-5.12	-1.99	3.13	4b	-5.15	-2.25	2.90
3c	-5.12	-2.02	3.10	4c	-5.28	-2.20	2.89
3d	-5.28	-2.58	2.70	4d	-5.30	-2.20	2.90
3e	-5.32	-2.42	2.90	4e	-5.41	-2.76	2.65
3f	-5.35	-2.87	2.48	4f	-5.42	-2.96	2.46

[a]Optical HOMO-LUMO gap

The influence of the peripheral groups on the electronic properties of the differently substituted hexaaryltriindoles is also clearly reflected in their spectroscopic behaviour. While absorption spectra of derivatives substituted with donor groups are almost identical, absorption spectra of derivatives substituted with acceptor groups show distinctive features of charge transfer: high extinction coefficients in the order of $10^5 \text{ M}^{-1}\text{cm}^{-1}$ and bathochromic shifts of the absorption maxima accompanied by a continuous loss of the vibronic fine structure of the respective band. Due to the electron rich character of the platform and its C_3 symmetry attachment of peripheral electron-withdrawing substituents results in compounds with a polar (octupolar) character.

On the other hand, as expected, extending the conjugation have a strong influence on the extension of the UV-vis absorption spectra of these derivatives showing a bathochromic shift when we compare for example derivatives substituted with equal peripheral groups but connected to the core by means of phenyl or phenylethynyl linker (Figure 5, compare spectra of **3c** and **4c**).

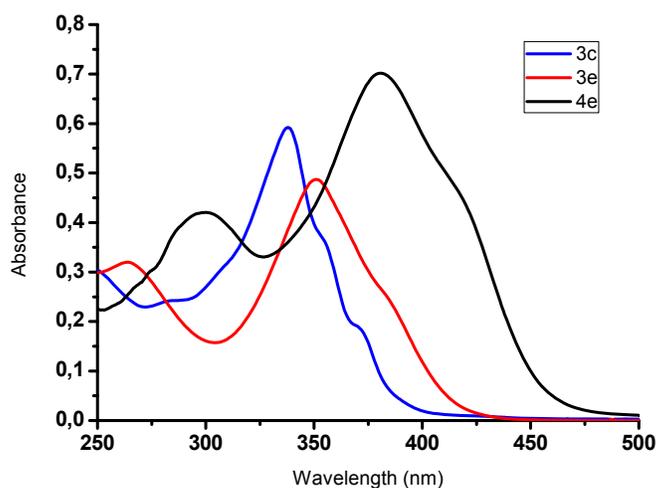


Fig. 5. UV spectra of **3c**, **3e** and **4e** in CH_2Cl_2 .

The dramatic influence that peripheral substituents of triindoles exert on their electronic properties of these derivatives offers a great opportunity to modulate their optical gap, again demonstrating the possibility of tuning the energy levels of these derivatives by chemical functionalization. Considering that organic electronic devices are usually constructed using multilayer architectures this possibility will be fundamental to facilitate charge injection from electrodes and minimize energy barriers between the different layers.

2.3. Structure-supramolecular organization relationships

We have also found that the electronic nature of the peripheral substituents has an influence in determining how these molecules interact with each other.^{5,6} A study of the electronic character of the peripheral substituents on their self-association behavior indicates that contrary to what is commonly observed, increasing the electron-donating character of the terminal substituents, facilitates self-association while electron-withdrawing groups inhibit aggregation. A study of the self-assembly process at different solvent compositions shows that upon the stacking tendency increases with the polarity of the solvent.

The unusual effect exerted by the substituents in the stacking tendency in this series of compounds is in agreement with a solvophobic-driven self-assembly. Increasing the polarity of the stacking surfaces would diminish their mutual repulsion

from the surrounding solvent and therefore their stacking propensity. The fact that self-association is sensitive to the polarity of the solvents, reinforce the contribution of solvophobic interactions in this particular case.

The design of molecules capable of organizing in a predictable way to form complex structures is a fundamental target of contemporary supramolecular and materials chemistry. In order to investigate how the solution behavior translates into molecular organization in solid state we have grown crystals triindole of two different derivatives showing opposed aggregation behavior in solution.

A close inspection of the molecular packing in these structures allows us to see that interestingly in the solid state these two derivatives show the same tendency observed in solution. While molecules of **3c** pack in the crystal forming dimeric aggregates, being the triindole units situated at 3.64 Å (average distance between centroids of the central aromatic rings of the platforms) molecules of **3e** pack in the crystal isolated by solvent molecules. Apparently solvent molecules effectively solvate the molecule, impeding π -stacking and showing the same behavior observed in solution, where interaction between the solute and the solvent will prevail over those between solute. This result allows us to visualize an unusual image of the solvophobic character of the self-assembly of this family of compounds

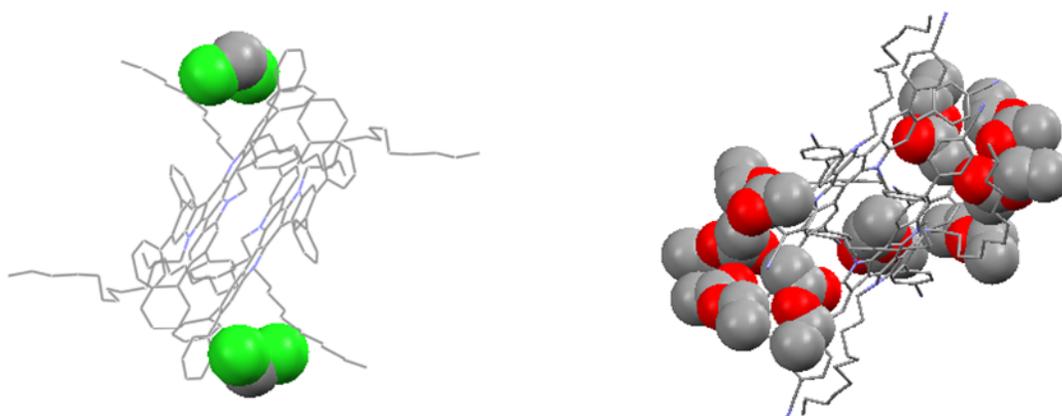


Fig. 6. Dimeric packing of **3c** (left) and **3e** (right).

These results suggest the possibility of tuning the intermolecular interactions between triindole units through a control of the electronic character of the peripheral substituents, as well as through the choice of the solvent, and provide interesting hints for the design of new triindole-based materials with improved self-assembly properties. It has been long demonstrated in the literature that self-assembled arrays formed in solution can be successfully transferred onto solid supports, resulting in highly oriented films with important implications in the development of molecule-based electronic devices.

2.4. Film-forming properties and applications to solution processed devices.

In spite that much advances have been made towards single crystal-based devices⁹⁻¹¹ their fragility difficult their processing and massive applications. In order to select the best candidates for practical applications we have study the film-forming properties of the new derivatives synthesized.

Films of triindole derivatives were prepared by spin coating from 1wt% dichloromethane as precursor solutions. Hexaphenyl derivatives **3** gave rise to the most homogeneous films. Apparently bulky phenyl groups impede crystallization facilitating the film-forming properties.

Solution processed diodes based on **3a** and **3d** have been fabricated and characterized for a preliminar study of the semiconducting properties of these materials. Compounds **3a** and **3d** have been selected considering their electronic properties as they offer two markedly different situation in terms of HOMO-LUMO levels, and due to their good film-forming properties. In particular we have fabricated organic light emitting devices (OLEDs) with a ITO/PEDOT:PSS/active layer/Al structure. With this arrangement, the HOMO-LUMO levels of the materials render these devices hole-dominated (Figure 7a). We observed threshold voltages of 17V and 15 V for **3a** and **3d**. This difference probably reflects the lower LUMO level for **3d** that improves electron injection. However, no emission was

observed from these devices pointing to inefficient adjustment between the Al cathode and LUMO level of the materials that gives rise to a very unbalanced injection of charge.

These preliminary results confirm that these materials are suitable for integrating as active layers in solution processed devices. Better energy levels alignments will result in better performing devices. Work along these lines is in progress.

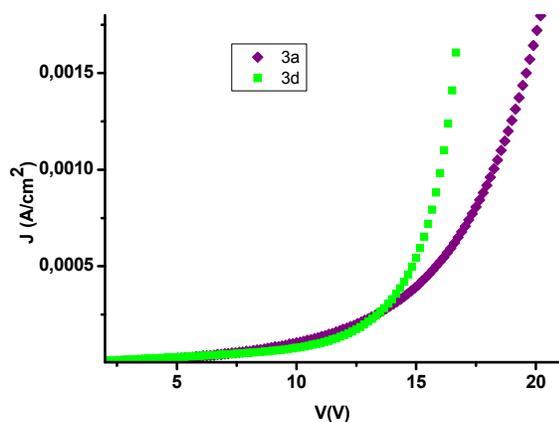


Fig. 7. a) Experimental J-V curve of **3a** and **3d**.

CONCLUSIONS

In conclusion we introduce a new family of stable high-mobility organic π -type semiconductors based on the π -conjugated electron-rich triindole platform. These compounds, present two different types of positions that can be functionalized independently offering the possibility of tuning their electronic properties as well as their morphology through chemical functionalization. The integration of the optimized triindole derivatives into solution processed devices as active layer is explored in this work.

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REFERENCES

- [1] Müllen, K., Scherf, U., "Organic Light-Emitting Devices. Synthesis, Properties and Applications", Wiley-VCH, Weinheim (2006).
- [2] Klauk, H., "Organic Electronics" Wiley-VCH, Weinheim, (2006).
- [3] Brabec, C., Dyakonov, V., Scherf, U., "Organic Photovoltaics", Wiley-VCH, Weinheim, (2008).
- [4] García-Frutos, E. M., Gutierrez-Puebla, E., Monge, M. A., Ramírez, R., de Andrés, P., de Andrés, A., Ramírez, R., Gómez-Lor, B., "Crystal structure and charge-transport properties of N-trimethyltriindole: Novel p-type organic semiconductor single crystals" *Org. Electr.* 10, 643-652 (2009).

- [5] García-Frutos, E. M., Gómez-Lor, B., “Synthesis and Self-Association Properties of Functionalized C_3 -Symmetric Hexakis(*p*-substituted-phenylethynyl)triindoles” *J. Am. Chem. Soc.* 190, 9173-9177(2008).
- [6] García-Frutos, E. M., Hennrich, G., Gutierrez, E., Monge A., Gómez-Lor, B., “Self-Assembly of C_3 -Symmetrical Hexaaryltriindoles Driven by Solvophobic and CH- π Interactions” *J. Org. Chem.* 75 (4), 1070-1076 (2010).
- [7] Gómez-Lor, B., Hennrich, G., Alonso, B., Monge, A., Gutierrez-Puebla, E., Echavarren, A. M. “Redox-active C_3 -Symmetric Triindole based Triazacyclophane” *Angewandte Chemie* 27, 4603-4606 (2006).
- [8] Bard, A. J., Faulkner, L. R., “Electrochemical Methods-Fundamentals and Applications”, Wiley, New York, (1980).
- [9] Briseno, A. L., Mannsfeld, S. C. B., Ling, M. M., Liu, S., Tseng, R. J., Reese, C., Roberts, M. E., Yang, Y., Wudl, F., Bao, Z., “Patterning organic single-crystal transistor arrays” *Nature* 444, 913-917(2006).
- [10] Li, R., Hu, W., Liu, Y., Zhu, D., “Micro- and Nanocrystals of Organic Semiconductors” *Acc.Chem. Res.* 43 (4), 529–540 (2010).
- [11] Liu, S., Wang, W. M., Briseno, A. L., Mannsfeld, S. C. B., Bao, Z., “Controlled Deposition of Crystalline Organic Semiconductors for Field-Effect-Transistor Applications” *Adv. Mater.* 21, 1217–1232, (2009).