

Quinacridone-Based Small Acceptor Molecule for Obtaining High Open Circuit Voltage in Solution Processed Organic Solar Cells

^{1,2,3} Iqbal Javed*, ⁴ Iqbal Saleem, ¹ Yue Wang, ³ Muhammad Nadeem Akhtar

¹State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China.

²Department of chemistry, Umeå University, SE-901 87 Umeå, Sweden.

³Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad, 38040, Pakistan.

⁴Institute of chemical Engineering and Technology, University of The Punjab, Lahore, 54590, Pakistan.

javedkhattak79@gmail.com, javed.iqbal@chem.umu.se, javed.iqbal@uaf.edu.pk

(Received on 3rd April 2014, accepted in revised form 23rd December 2014)

Summary: Dioctylquinacridone di(cyanoimine) CN-DOQA was synthesized according to previously reported method. CN-DOQA having suitable HOMO-LUMO energy levels due to -CN groups as electron withdrawing groups was used in organic solar cells as an acceptor in a blend with poly (3-hexyl thiophene) (P3HT) as donor. The photovoltaic devices have shown reasonable high open circuit voltage (Voc) although solar cells have not been fully optimized. Photovoltaic study was supported by thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC) of CN-DOQA and morphological study of the blend films by atomic force microscopy (AFM).

Key Words: Quinacridone, Acceptor, Heterojunction solar cells, Open Circuit Voltage, TGA, DSC, AFM.

Introduction

Solar cells based on organic materials have substantial potential for future applications due to the low cost in both materials and device fabrication. A number of new-generation solar cells are currently under investigation, including dye-sensitized solar cells (DSSCs) [1], polymer/fullerene bulk heterojunction (BHJ) solar cells [2], and vapor deposited small molecule solar cells [3]. More recently, solution-processed solar cells using soluble small molecules have attracted great attention for their numerous attractive features, i.e., high molecular purity, reproducibility and scalable synthesis, tunable optoelectronic properties through structural control, high carrier mobility, and excellent stability [4, 5]. Herein, we report our efforts in exploring a new class of molecular acceptor materials based on a well-known organic pigment core of quinacridone.

Quinacridone and its derivatives (QA) are well-known organic pigments [6] and dopant emitters [7] that show excellent chemical stability and fastness properties as well as pronounced photovoltaic and photoconductive activities [8-10]. Because of good electrochemical stability in the solid state and high photoluminescent efficiency in dilute solution, quinacridone and its derivatives are promising materials for fabricating high-performance organic light-emitting devices (OLEDs). A great deal of effort has been invested in the optimization of QA-based devices in terms of efficiency and lifetime [11-13]. Although a lot of studies have been made on

quinacridone and its derivatives for its use in OLED and other applications successfully, a little attention has been paid for the possibility of their use in the photovoltaic devices. The photoconductivity of quinacridones has been reported in a few vapor deposited organic solar cells back in 1980s [14, 15]. QA molecular structure can be varied by substitution of carbon atoms by 'N' and 'O'. QA can also be modified by attaching lateral alkyl chain to 'N' heteroatom and by the formation of QAnC, where 'n' denotes the number of carbon atoms in the alkyl chain. In our previous work we introduced a new type of QA derivatives by replacing carbonyl oxygen of QA by some substituents [16].

Recently quinacridone derivatives have been successfully used as donor material in small molecular based organic solar cells [17]. Many efforts have been put forward to design the donor materials; however, search for new acceptor materials is quite limited. Herein quinacridone di(cyanoimine) (CN-DOQA) derivative was synthesized by condensation of alkyl substituted quinacridones with aromatic amine according to our previously reported method [18]. Cyano groups are introduced as electron withdrawing groups and aniline base as backbone for good conducting properties. This material has been used in blend with one of the most efficient donor poly (3-hexyl thiophene) (P3HT). The photovoltaic devices based on this donor-acceptor combination have shown reasonable photovoltaic properties although preparation process of solar cells has not

*To whom all correspondence should be addressed.

been fully optimized. Photovoltaic study of the devices is supported by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) of the compound and morphological study of the blend films by atomic force microscopy (AFM).

Experimental

Instrumentation: ^1H NMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal standard. Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter. UV-vis absorption spectra were recorded using a PE UV-vis lambdaDSCO spectrometer.

Electrochemical Measurements: Cyclic voltammetry was performed on a BAS 100W instrument with a scan rate of 100mV/s. A three-electrode configuration was used for the measurement: a platinum electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode. A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in CH₂Cl₂ was used as the supporting electrolyte.

Solar Cell Fabrication: The ITO-coated glass substrates were ultra-sonicated for 20 min each in toluene, acetone and then in 2% Hellmanex soap water, followed by extensive rinsing and ultrasonication in deionized water and then isopropyl alcohol. The substrates were then dried under a stream of dry nitrogen. A dispersion of PEDOT: PSS (Baytron PH500) in water was filtered (0.45 μm glass) and spin coated at 4000 rpm for 60 s, affording a ~ 30 nm layer. The substrates were dried for 60 min at 120 C° in air at hot plate. Blend solutions were prepared in 1, 2-dichlorobenzene by taking 8 mg of P3HT and 8 mg of QA derivative in 1 mL and were stirred for 48 hours for complete dissolution. The active layer was spin coated at 900 rpm for 60 s on top of the PEDOT: PSS layer and dried in vacuum (10⁻² torr) to remove residual P3HT. The substrates were then placed in an evaporation chamber and pumped down to a pressure of ~ 5 × 10⁻⁴ torr before evaporating a 1 nm LiF layer and subsequently a 100 nm Al layer through a shadow mask on top of the photoactive layer. The mechanical removal of part of the organic layer allowed contact with the ITO and adding conductive Ag paste to the removed area to ensure electrical contact completed the device. Devices were annealed by placing on hot plates for 12 min at 60 C°.

Characterization: Testing of the devices was performed in ambient atmosphere with an Oriel Xenon arc lamp having an AM 1.5G solar filter to yield 100 mWcm⁻² light intensity as calibrated by an NREL certified silicon photocell. Current-voltage behavior was measured with a Keithley 236 SMU.

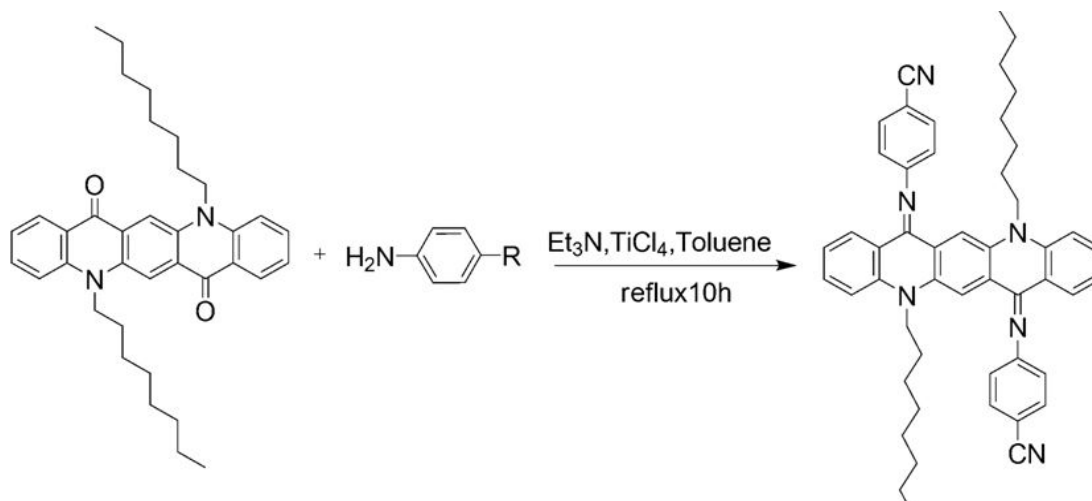
Synthesis: Quinacridone was purchased from Tokyo Kasei Kogyo Company. Cyanoaniline and 1-bromooctane were obtained from Acros Organics. The chemicals were used directly without further purification. N,N-di(n-onyl)quinacridone (DOQA) was synthesized according to standard procedures [19]. Quinacridone di(cyanoimine) (CN-DOQA) is synthesized as follow according to our previous reported procedure [18].

p-cyanoaniline (4 mmol) and triethylamine (TEA) 1.2mL (8.5 mmol) were dissolved in 20 mL toluene. Titanium chloride (TiCl₄) 0.6 mL (5.4mmol) in 5 mL toluene was added drop wise over 15 min by addition funnel. The addition funnel was rinsed with 3 mL toluene. DOQA (1 mmol) was added by powder addition funnel at once. The funnel was rinsed with 3 mL toluene. The reaction mixture was refluxed for about 10 hours. The reaction mixture was cooled and filtered, the filtrate obtained was dried and loaded on silica gel column and eluted with CH₂Cl₂: Diethyl ether (50:1). The desired product was obtained as a red solid in a 60% yield.

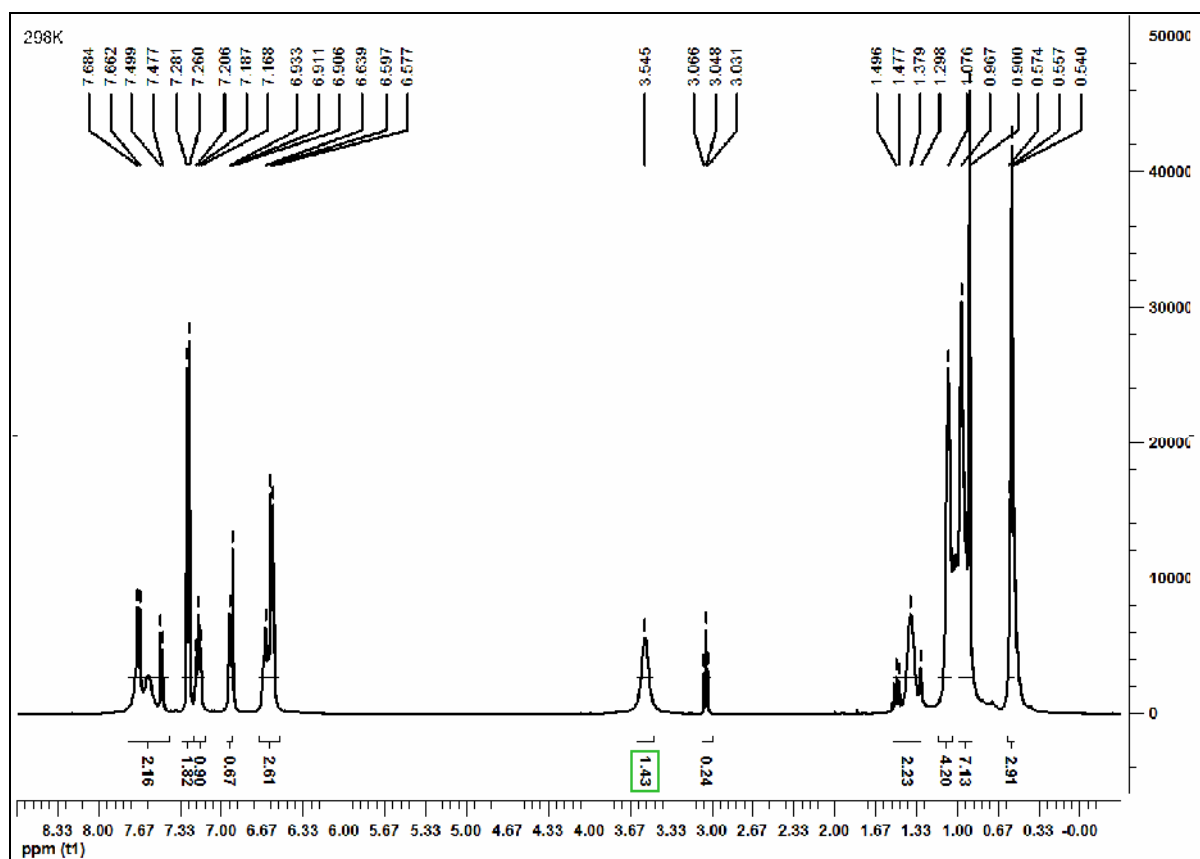
^1H NMR (CDCl₃, ppm) (500MHz): δ 7.83-8.04 (m, 4H), 7.62 (d, 8H), 7.53 (t, 2H), 7.28 (s, 2H), 6.95(t, 6H), 3.89-4.38 (m, 4H), 1.73-2.00 (m, 4H), 1.31-1.42 (m, 22H), 0.90 (t, 4H), MS: m/z 736.20[M]⁺. Anal. Calcd for C₅₀H₅₂N₆; C, 81.49; H, 7.11; N, 11.40. Found: C, 81.15; H, 6.99; N, 11.41.

Result and Discussion

Synthesis: The synthetic procedure is outlined in Scheme-1. Alkyl substituted quinacridones were synthesized according to the standard procedure. Introduction of alkyl chain prevents the hydrogen bonding between C=O and N-H, therefore solubility of quinacridone is increased. The soluble alkyl substituted quinacridones were treated with aromatic amine (cyanoaniline) to form electron accepting quinacridones derivative. The compound is soluble in common organic solvents, such as toluene, chloroform and tetrahydrofuran (THF) etc. The chemical structures were verified by ^1H -NMR, mass spectrometry and element analysis.



Scheme-1: Synthesis procedure of CN-DOQA from DOQA.

Fig. 1: $^1\text{H-NMR}$ spectrum of CN-DOQA.

Redox Properties

Cyclic voltammetry (CV) was performed in anhydrous CH_2Cl_2 solution with 0.1 M TBAP as supporting electrolyte (Fig. 2).

CN-DOQA exhibits reversible reduction and oxidation wave potential. The first half wave reduction and oxidation potentials of the compound is

($E_{\text{red}}^{1/2} = -1.14\text{V}$) and ($E_{\text{ox}}^{1/2} = 0.76\text{V}$) respectively. The electrochemical information gives unclouded picture of the effect of electron withdrawing groups on electrochemistry of the compound. This effect is also translated in the LUMO and HOMO levels; compound has relatively lower LUMO and HOMO levels.

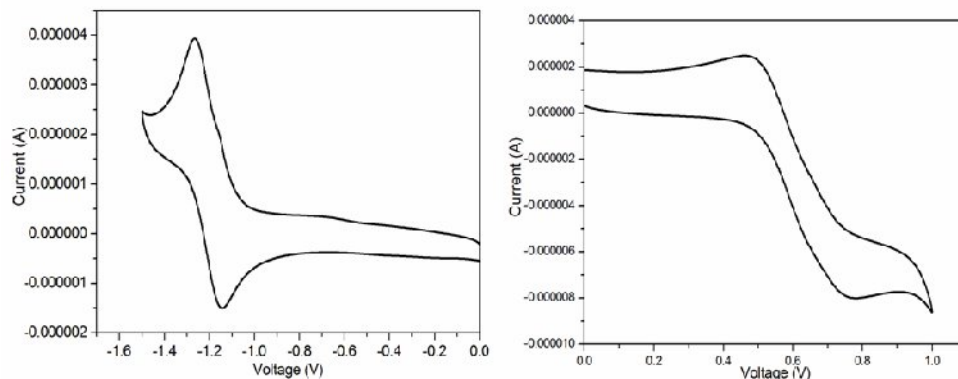


Fig. 2: Cyclic voltammograms of CN-DOQA recorded in CH_2Cl_2 with scan rate of 100mVs^{-1}

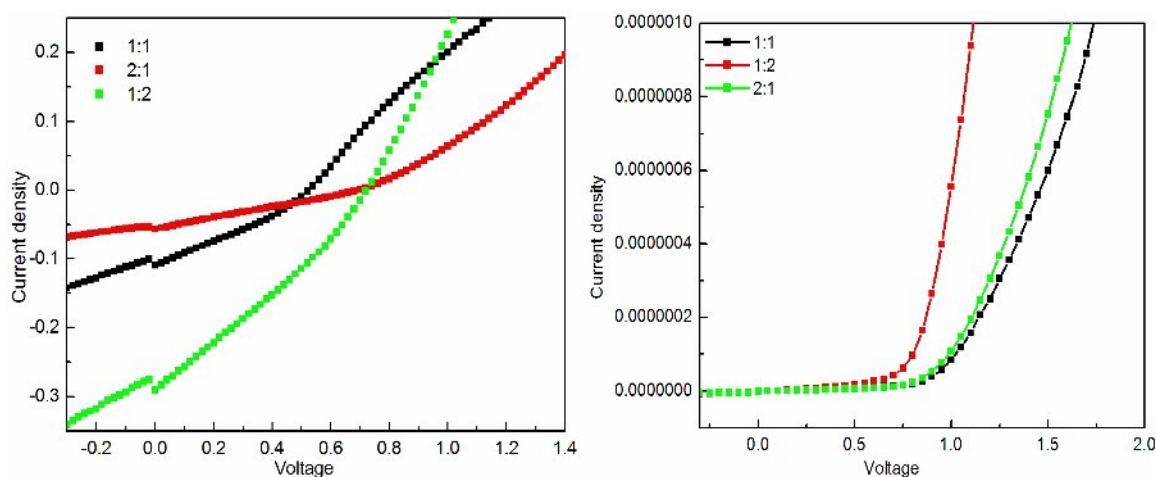


Fig. 3: J-V curve of ITO/PEDOT/P3HT: CN-DOQA (1:1, 2:1, 1:2)/LiF/Al devices under $100\text{mW}/\text{cm}^2$ White illumination (left) and in dark (right Application in Organic Solar Cells)

By carefully examining Photophysical and electrochemical properties of CN-DOQA it is deduced that it could be a good candidate as an acceptor in organic solar cell with suitable donor material. We fabricated CN-DOQA from the blend with effective polymer donor P3HT in dichlorobenzene by spin coating and blend solutions were prepared in 1, 2-dichlorobenzene with different ratios. The solar cells were fabricated with the structure of ITO/PEDOT-PSS/P3HT: CN-DOQA /LiF/ Al and the measurements of the performance were conducted at ambient atmosphere. Before measuring photovoltaic properties all the devices were annealed at $60\text{ }^\circ\text{C}$ for 12 minutes. (Fig. 3) shows the I-V curves of the solar cell devices under AM 1.5 conditions with $100\text{mW}/\text{cm}^2$. Representative characteristics of the solar cells are listed in (Table-1). It is worth noting that devices with same ratios of donor and acceptor have relatively low V_{oc} . Devices fabricated with 1:2 ratio of donor to acceptor show higher performance ($\eta = 0.063\%$) with V_{oc} of 0.76

V. It is worth noting that as the concentration of the acceptor is increased we found photocurrent to be increased. This may be due to increase in interfacial area and corresponding percolation opportunity for whole transport through bulk of active layer.

Table-1: Summary of device performance (AM1.5G, $100\text{mW}/\text{cm}^2$) for various types of solar cells fabricated in this work.

P3HT:CN-DOQA	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
1:1	0.12	0.52	30	0.019
1:2	0.28	0.76	29	0.063
2:1	0.069	0.72	25	0.012

Absorption of Blend Film

Fig. 4 shows the optical spectra of neat CN-DOQA, neat P3HT film and blend films. The spectrum of blend films covers wide range of absorption band (370–650 nm) with prominent peaks at 489, 549, 553 and 602 nm. It looks like superimposition of the two component spectra which is

one of the limiting factors of low power conversion efficiency. The spectral peaks of (2:1) blend film are more intense than (1:2) and (1:1) blend film and the peaks mainly correspond to neat P3HT spectral peaks as P3HT is the major components of this blend film. In case of (1:1) and (1:2) blend film spectra the λ_{max} of CN-DOQA is red shifted from 542 nm to 549 nm in blend film which is possibly due to favorable aggregation of the components.

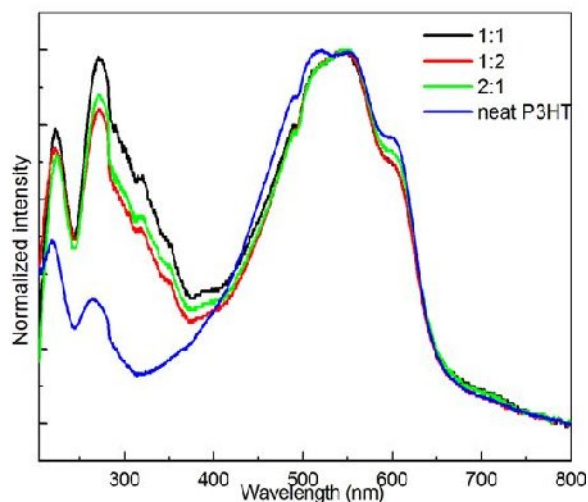


Fig. 4: Absorption spectra of blend film and neat P3HT

The thermal properties of CN-DOQA was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min (Fig. 5). TGA analysis shows that the compound is thermally stable, although it loses 2% of its total mass at ~ 209 C° but afterward its weight remains constant until ~339 C°. The decomposition temperature with 5 % loss ($T_{\text{d}5}$) is 355 C° which indicates that CN-DOQA is thermally stable. This is crucial on the encapsulation of the electronic devices because this can endure high temperature and resist the penetration of gas despite the electronic device liberates much heat when actuated [20].

DSC curve gave some interesting information. There are two exothermic peaks, one sharp peak at 125 C° and other very small peak at 151 C° which indicates that compound may have different crystalline forms as indicated in our previous report [18]. Similarly there are two melting temperatures at 180 C° and 195 C°. The property of crystallization is beneficial for applications in organic solar cells since a highly ordered heterojunction nanostructure enhanced by the crystallization of compound in PV layer is desirable for charge separation and transport [21].

Thermal Analysis

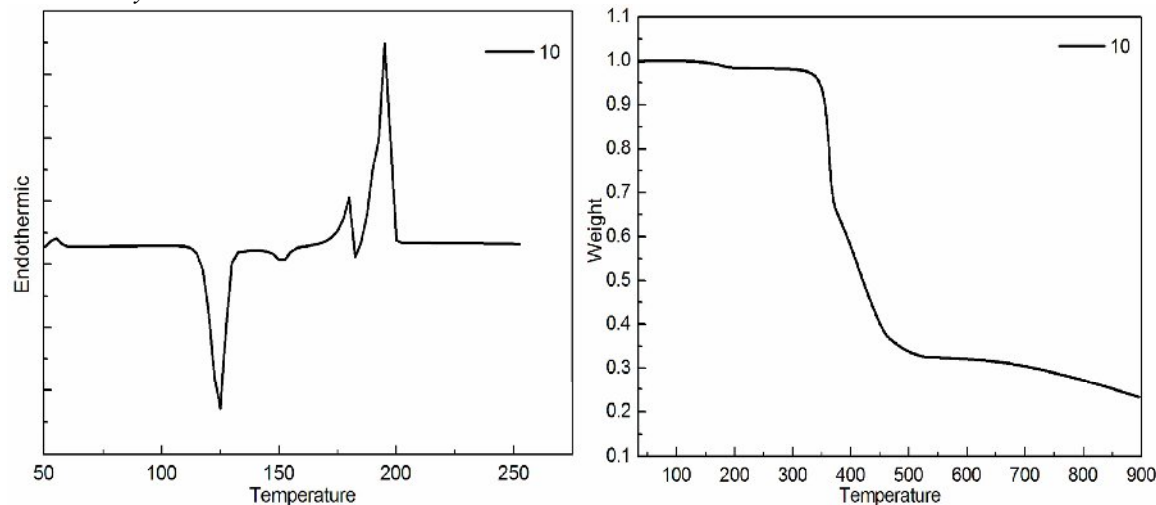


Fig. 5: Thermogravimetric analysis (TGA) (right) and Dynamic scanning calorimetry (DSC) (left) of CN-DOQA.

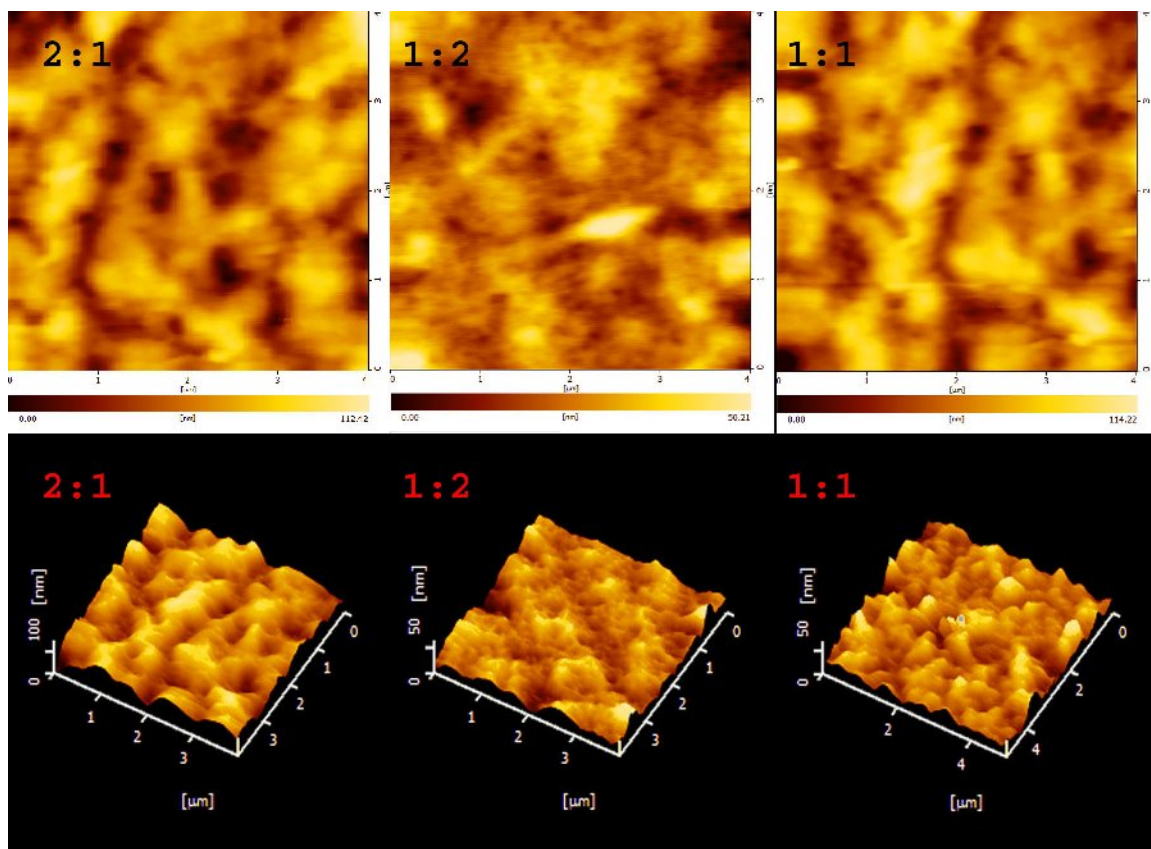


Fig. 6: AFM height images of blend films ($5.0\mu\text{m} \times 5.0\mu\text{m}$) tapping mode.

Morphology Study

Morphology of heterojunction solar cells affects all aspects of photovoltaic performance including charge generation, charge separation, and charge transport. This is baffling, since morphology is itself a complex phenomenon and can be challenging to predict or control experimentally. The typical heterojunction morphology is essentially a metastable state that is frozen in at the end of the drying process, although further morphology evolution can be provided by thermal or solvent-vapor annealing [12, 22]. Additional factors that influence the morphology are molecular weight [21], regioregularity of polymer [23], solvent [24], side chain length [25], and weight percentage [26]. Since heterojunction morphology is sensitive to many factors, so, the domain size and packing are not always uniform throughout the film.

AFM images (Fig. 6) show the film with 2:1 and 1:1 ratios have large scale phase separation as compared to the film with 1:2 ratio. All the films have rough surface which is also a limiting factor for

higher efficiency. The root mean square roughness (rms) values for (1:2), (2:1) and (1:1) are 24.56, 59.02 and 91.90 nm respectively.

Conclusion

CN-DOQA with suitable HOMO-LUMO energy levels due to $-\text{CN}$ groups as electron withdrawing groups was used in organic solar cells as an acceptor in a blend with poly (3-hexyl thiophene) (P3HT) as donor material. The photovoltaic devices have shown reasonable properties especially high Voc, although solar cells have not been fully optimized. Photovoltaic study was supported by thermogravimetric analysis (TGA) dynamic scanning calorimetry (DSC) of CN-DOQA and morphological study of the blend films by atomic force microscopy (AFM). Although great deal of efforts are in progress for new photovoltaic materials but our work will open new horizons in designing novel photovoltaic materials based on quinacridones by carbonyl functionalization after introducing special structural units on QA skeleton for avoiding buckling and non-planarity of the molecules.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (50773027 and 50733002), the Major State Basic Research Development Program (2009CB939700), and 111 Project (B06009). Author also acknowledges Umea University, Umea, Sweden for NMR facilities.

References

1. B. O'Regan and M. Grätzel, A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films, *Nature*, **353**, 737 (1991).
2. G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions, *Science*, **270**, 1789 (1995).
3. C. W. Tang, Two-Layer Organic Photovoltaic Cell, *Appl Phys Lett*, **48**, 183 (1986).
4. M. Lloyd, J. Anthony and G. Malliaras, Photovoltaics from Soluble Small Molecules, *Mater. Today*, **10**, 34 (2007).
5. J. Roncali, Molecular Bulk Heterojunctions: An Emerging Approach to Organic Solar Cells, *Acc Chem Res*, **42**, 1719 (2009).
6. M. Hiramoto, S. Kawase and M. Yokoyama, Photoinduced Hole Injection Multiplication in p-Type Quinacridone Pigment Films, *Japanese J. of Appl Phys*, **35**, L349 (1996).
7. G. E. Jabbour, Y. Kawabe, S. E. Shaheen, J. F. Wang, M. M. Morrell, B. Kippelen, N. Peyghambarian, Highly Efficient and Bright Organic Electroluminescent Devices with an Aluminum Cathode, *Appl Phys Lett*, **71**, 1762 (1997).
8. H. Nakahara, K. Fukuda, M. Ikeda, K. Kitahara, H. Nishi, Langmuir-Blodgett-Films of Polyheterocyclic Compounds with Long Alkyl Chains, *Thin Solid Films*, **210**, 555 (1992).
9. T. Shichiri, M. Suezaki and T. Inoue, Three-Layer Organic Solar Cell, *Chem Lett.*, 1717 (1992).
10. J. M. Shi, C. W. Tang, Doped Organic Electroluminescent Devices with Improved Stability, *Appl Phys Lett*, **70**, 1665 (1997).
11. S. E. Shaheen, B. Kippelen, N. Peyghambarian, J. F. Wang, J. D. Anderson, E. A. Mash, P. A. Lee, N. R. Armstrong and Y. Kawabe, Energy and Charge Transfer in Organic Light-Emitting Diodes: A Soluble Quinacridone Study, *J. Appl Phys*, **85**, 7939 (1999).
12. E. M. Gross, J. D. Anderson, A. F. Slaterbeck, S. Thayumanavan, S. Barlow, Y. Zhang, S. R. Marder, H. K. Hall, M. F. Nabor, J. F. Wang, E. A. Mash, N. R. Armstrong, R. M. Wightman, Electrogenerated Chemiluminescence from Derivatives of Aluminum Quinolate and Quinacridones: Cross-Reactions with Triarylaminines Lead to Singlet Emission through Triplet-Triplet Annihilation Pathways, *J. Am. Chem. Soc.*, **122**, 4972 (2000).
13. H. Aziz, Z. D. Popovic, N. X. Hu, Organic Light Emitting Devices with Enhanced Operational Stability at Elevated Temperatures, *Appl. Phys Lett*, **81**, 370 (2002).
14. M. Tomida, S. Kusabayashi, M. Yokoyama, Organic Solar Cell Fabrication using Quinacridone Pigments, *Chem. Lett*, **8**, 1305 (1984).
15. K. Manabe, S. Kusabayashi and M. Yokoyama, Long-Life Organic Solar Cell Fabrication Using Quinacridone Pigment, *Chem. Lett*, **4**, 609 (1987).
16. I. Javed, Z. Zhang, T. Peng, T. Zhou, H. Zhang, M. Issa Khan, Y. Liu and Y. Wang, Solution Processable Quinacridone based Materials as Acceptor for Organic Heterojunction Solar Cells, *Sol. Energy Mat. & Sol Cells*, **95**, 2670 (2011).
17. J. J. Chen, T. L. Chen, B. Kim, D. A. Poulsen, J. L. Mynar, J. M. Frechet and B. Ma, Quinacridone-Based Molecular Donors for Solution Processed Bulk-Heterojunction Organic Solar Cells, *ACS Appl Mater Interfaces*, **2**, 2679(2010).
18. I. Javed, A. Khurshid, M. N. Arshad, Y. Wang, Photophysical and Electrochemical Properties and Temperature Dependent Geometrical Isomerism in Alkyl Quinacridonediiimines, *New.J. Chem*, **38**, 752 (2014).
19. S. De Feyter, A. Gesquière, F. C. De Schryver, U. Keller, K. Müllen, Aggregation Properties of Soluble Quinacridones in Two and Three Dimensions, *Chem Mater*, **14**, 989 (2002).
20. C. Chen, M. Chung, T. Hsieh, M. Liu, J. Lin, W. Chu, R. Tang, Y. Tsai, F. Juang, Synthesis, Thermal Characterization, and Gas Barrier Properties of UV Curable Organic/Inorganic Hybrid Nanocomposites with Metal Alloys and their Application for Encapsulation of Organic Solar Cells, *Comp Sci &Tech.*, **68**, 3041 (2008).
21. W. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology, *Adv Func Mater*, **15**, 1617 (2005).
22. X. Yang, J. Loos, S. C. Veenstra, W. J. Verhees, M. M. Wienk, J. M. Kroon, M. A. Michels, R. A. Janssen, Nanoscale Morphology of High-Performance Polymer Solar Cells, *Nano Lett*, **5**, 579 (2005).

23. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, M. Ree, A Strong Regioregularity Effect in Self-Organizing Conjugated Polymer Films and High-Efficiency Polythiophene:Fullerene Solar Cells, *Nature Materials*, **5**, 197 (2006).
24. A. C. Arias, J. D. MacKenzie, R. Stevenson, J. J. M. Halls, M. Inbasekaran, E. P. Woo, D. Richards, R. H. Friend, Photovoltaic Performance and Morphology of Polyfluorene Blends: A Combined Microscopic and Photovoltaic Investigation, *Macromolecules*, **34**, 6005 (2001).
25. L. H. Nguyen, H. Hoppe, T. Erb, S. Günes, G. Gobsch, N. S. Sariciftci, Effects of Annealing on the Nanomorphology and Performance of Poly(alkylthiophene):Fullerene Bulk-Heterojunction Solar Cells, *Adv Func Mater*, **17**, 1071 (2007).
26. J. K. J. Van Duren, X. Yang, J. Loos, C. W. T. Bulle-Lieuwma, A. B. Sieval, J. C. Hummelen, R. A. J. Janssen, Relating the Morphology of Poly(p-phenylene vinylene)/Methanofullerene Blends to Solar-Cell Performance, *Adv Func Mater*, **14**, 425 (2004).