View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Suman, A. Bagui, R. dutt, V. Gupta and S. P. Singh, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC08237A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 06 November 2017. Downloaded by Northwestern University on 07/11/2017 01:05:15.

YAL SOCIETY CHEMISTRY

Journal Name

COMMUNICATION

A Simple Fluorene Core-Based Non-fullerene Acceptor for High **Performance Organic Solar Cells**

Received 00th January 20xx, Accepted 00th January 20xx

Suman^{a,b}, Anirban Bagui^a, Ram Dutt,^c Vinay Gupta^c, and Surya Prakash Singh^{*a,b}

DOI: 10.1039/x0xx00000x

www.rsc.org/

A small molecule non-fullerene acceptor based on fluorene core having furan π -spacer and end capped with rhodanine (FRd₂) is developed for solution processable bulk heterojunction organic solar cells (OSCs). The simplistic synthtic protocol reduces several reaction steps and hence production cost. Extended π-conjugation via furan units and presence of electronegative rhodanine groups result in a power conversion efficiency of 9.4% in OSC, which is highest so far among these categories of molecules.

Small molecule non-fullerene acceptors (SMNFAs) are being used as potential alternative to conventional fullerene derivatives for fabrication of solution processable organic solar cells (OSCs). These molecules have advantages of easily tunable frontier molecular orbital (FMO) energy levels, strong broad spectral absorption, good thermal and and photochemical stability, low production cost and easy purification.¹ Till date, considerable research efforts have been made to develop varieties of SMNFAs and power conversion efficiencies (PCEs) over 13% have been achieved from OSCs made with these molecules.² Fluorene, which is a weak electron donating moiety, is widely used for the synthesis of broad range of materials for applications in organic electroluminescent devices, thin film transistors and solar cells due to the advantages of their high fluorescence quantum yield, excellent hole transport mobility and good thermal and chemical stability.³ More recently, fluorene moiety has been introduced as an excellent building block to synthesize p-type semiconductors for solution processable organic photovoltaics (OPVs).⁴ Two side alkyl chains at 9th position of fluorene improves solubility of the resultant molecule, whereas the deeply lying HOMO energy level of fluorene derivatives helps in achieving high open circuit voltage (V_{oc}) in OSCs.⁵ The optical band gap of these molecules can be easily tuned by extending linear π -conjugation.⁶ Usually the calamitic type SMNFAs contain a central donor unit (D) flanked with a second donor or, acceptor (D/A) unit and truncated with acceptor groups (A). A significant progress has been made in past few years in the

² CSIR-National Physical Laboratory, New Delhi-110012, India.

development of high performance SMNFAs with A-D/A-D-D/A-A structural configuration. However most of the reports were focused on changing the central core to improve the photovoltaic performance of acceptors. It is well known that incorporation of π -spacers such as thiophene, benzene, furan etc. also plays important role in increasing π -conjugation through molecular backbone and thus enhances the performance of molecules.⁷ Among the previously reported SMNFAs, fluorene core based acceptors were found to be most frequently explored due their effective light harvesting property in the visible range of 300 to 650 nm, easy synthesis and purification, as well as chemical and thermal stability. Many fluorene based materials, using benzothiadiazole and thiophene as π -spacer flanked with different dye end groups have been developed as small molecule acceptors for organic solar cell applications and achieved a power conversion efficiency of up 8.4%.8 To design highly efficient SMNFAs, integration of appropriate electron deficient groups such as rhodanine,¹¹ malononitrile,9 rhodanine,¹⁰ dicyano 1,1-dicyanomethylene-3-indanone,¹³ diketopyrrolopyrrole,¹² perylene diimide,¹⁴ is also very important, which improves the light absorption properties, lowers the energy of LUMO level, increases the probability of exciton dissociation at the donoracceptor interface and consequently enhances the performance of an electron acceptor. Benzothiadiazole is an easily synthesizable electron withdrawing group, which is widely used to design not only donor and acceptor polymers, but also for synthesis of small molecules. Incorporation of benzothiadiazole moiety increases electron deficiency in the resultant molecule. Introduction of furan unit in π -conjugated backbone extends conjugation and lowers the enrgy bandgap of final molecule. Therefore the absorption spectrum of the molecule is expected to shift towards longer wavelength (red shift). Rhodanine is an electron withdrawing moiety, increase the electron deficient property at the end of molecule via its ketone and thioketone groups. Ethyl group at the nitrogen of rhodanine increase the solubility and inhibit the hydrogen bonding of molecule.



^{a.} Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal road, Tarnaka, Hyderabad-500007, India. Email: spsingh@iict.res.in

^{b.} Academy of Scientific and Innovative Research.

DOI: 10.1039/C7CC08237A Journal Name

COMMUNICATION

Published on 06 November 2017. Downloaded by Northwestern University on 07/11/2017 01:05:15.

Hence, our group designed and synthesized SMNFA (FRd₂) with extended π -conjugation using furan as spacer and rhodanine as terminal units associated with fluorene core for solution processable OPVs (Fig. 1). The synthetic protocol of final product, i.e. \mathbf{FRd}_2 and intermediates are outlined in scheme S1. A detailed synthetic procedure and characterization results are also provided in ESI. The dialdehyde intermediate (F₂CHO) was synthesized by Suzuki cross coupling reaction between 2,7-diboronic ester of fluorene (BAF-BA₂) and 5-(7-bromobenzo[c][1,2,5]thiadiazole-4-yl)furan-2-carbadehyde (BT-F-CHO). The final molecule FRd₂ was prepared by Knoevenagel condensation reaction of dialdehyde intermediate (F₂CHO) with 3-ethylrhodanine. All intermediates and target molecule were fully characterized by NMR, FT-IR and MALDI-TOF spectroscopy (Fig. S1-S8). The new molecule exhibits good solubility (10 mg/mL) in common organic solvent such as dichloromethane, chloroform, chlorobenzene and tetrahydrofuran.



The normalized absorption spectra of $\mathbf{FRd_2}$ in chloroform solution and thin film are exhibited in **Fig. 2**. A broader absorption profile was observed in thin film compared to that in solution because of higher delocalization in solid state. The new SMNFA showed a strong and broad absorption in the range of 300-620 nm with highest molar extinction coefficient of 4.9×10^4 Mol⁻¹cm⁻¹ at 509 nm. The absorption profile of **FRd_2** shows two peaks at 414 and 509 nm due to the π - π * transition and internal charge transfer from central fluorene molecule (donor) to terminal acceptor units, respectively. It is noteworthy to mention that absorption range of PTB7-Th and **FRd_2** are complementary to each other. Hence both of them are expected to contribute in photocurrent. The PTB7-Th:**FRd_2** blend also showed a broad absorption profile extending up to 870 nm.

The electrochemical properties of FRd_2 were investigated by cyclic voltammetry using Fc/Fc^+ redox couple as internal standard (**Fig. S9**). The HOMO energy level of acceptor molecule is calculated from the onset oxidation potential and found to be -5.67 eV. The optical band gap of **FRd**₂ is 2.09 eV as measured from the onset of the absorption spectrum. The

LUMO energy level of molecule, estimated from the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$, is found to be -3.58 eV (**Table S1**). Introducing furan π -spacer in the acceptor molecule extends π -conjugation, thus reduces band gap and lowers LUMO energy level, which in turn expected to help in device performance.

Theoretical calculation of FMO energy levels (section S5, Fig. S10) reveals that the HOMO is evenly distributed on entire molecule, whereas LUMO is more concentated at the perifery of molecule. This configuration helps in accepting electron easily from the donor molecule.



Fig. 2 Normalized UV-visible absorption spectra of FRd_2 along with its blend thin films with PTB7-Th.

The photovoltaic properties of new acceptor were studied constructing BHJ OSCs in inverted device structure-ITO/ZnO/PTB7-Th:FRd2/MoO3/Ag. A detailed fabrication process is described in supporting information. The schematic representations of device structure and energy level diagrams are depicted in the inset of Fig. 3a and b, respectively. During optimization of fabrication steps, effect of thermal annealing (TA), solvent vapor annealing (SVA) and solvent additives on device performance was also investigated. Chloronaphthalene (CN) and diiodooctane (DIO) were primarily chosen as additives in order to check the compatibility with new acceptor. Figure 3a represnts the characteristics J-V curves of the OSCs measured under 1 sun illumination (1000 W·m⁻²) using AM 1.5G filter. Solution processed BHJ OSCs made from 'as cast' PTB7-Th:FRd₂ blend showed a PCE of 6.4% with a Voc of 0.835 V, short circuit current density (J_{sc}) of 13.3 mA·cm⁻² and fill factor (FF) of 57.8%. The PCE increased to 6.9% with TA treatment of the photoactive layer without using any solvent additive. The devices made from 'thermally annealed' PTB7-Th:FRd₂ blends using CN as additive yielded a PCE of 7.2% with a V_{oc} of 0.836 V, J_{sc} of 13.9 mA cm⁻² and FF of 62.2%. However, DIO additive appeared to be more compatibile with FRd₂ molecule than CN. The OPV devices fabricated from thermally annealed PTB7-Th:FRd2 blends demonstrated a maximum PCE of 8.1%. As can be seen from Fig. 3a and Table 1, a noticeable improvement in the photovoltaic performance of BHJ OSCs was achieved upon SVA treatment of DIO added photoactive layer. This category of devices showed a highest PCE of 9.4% with increased J_{sc} of 15.7 mA·cm⁻², FF of 72.3% and V_{oc} of 0.833 v

Published on 06 November 2017. Downloaded by Northwestern University on 07/11/2017 01:05:15.

View Article Online DOI: 10.1039/C7CC08237A COMMUNICATION

Journal Name

The external quantum efficiency (EQE) spectra of OPV devices fabricated under different conditions are presented in **Fig. 3b**. The photon to current response curves of PTB7-Th:**FRd**₂ based devices exhibited a strong photo-response in the wavelength range of 350-750 nm. The BHJ solar cells made from thermally annealed PTB7-Th:**FRd**₂ active layer using DIO as additive showed an EQE over 70% at 710 nm. The EQE value further increased to 75% with SVA treatment of blend films.



Fig. 3 (a)The light J-V characteristics of champion devices made from PTB7-Th:FRd₂ blend, inset: device structure of non fullerene BHJ organic solar cell fabricated in this work and (b) External quantum efficiency (EQE) of PTB7-Th:FRd₂ blend film.

Table 1. Summary of device performance parameters of polymer OSCs based on PTB7-Th:FRd₂ blend films.

NFAs	Additive	Treatments	J_{sc}	Voc	FF	PCE
			(mA/cm ²)	(V)	(%)	(%)
-	-	As cast	13.3	0.835	57.8	6.4 (6.2)*
PTB7-	-	TA	13.5	0.830	61.7	6.9 (6.6)
Th:	CN	TA	13.9	0.836	62.2	7.2 (7.0)
FRd ₂	DIO	TA	14.4	0.831	67.6	8.1 (7.9)
	DIO	SVA	15.7	0.833	72.3	9.4 (9.2)

*Average efficiencies are given in the parenthesis.

The charge carrier mobility in blend film was investigated constructing 'hole only' (ITO/PEDOT:PSS/blend/Au) and 'electron only' (ITO/*ZnO*/blend/Al) devices (**Fig. 4a, Fig. S11** and **Table S3**). The values of charge carrier mobility are estimated using Mott-Gurney's space charge limited current (SCLC) model at higher voltages.¹⁵ The electron mobility (μ_e) of **FRd₂** in the blend is calculated to be 2.5×10⁻⁴ and 4.3×10⁻⁴ cm²V⁻¹s⁻¹ for TA and SVA treated films, respectively. The hole mobility (μ_h) of PTB7-Th in blend also increases with SVA treatment. Interestingly, μ_e and μ_h become more well-balanced with SVA treatment. The μ_e/μ_h ratio improves from 1.92 for TA to 1.79 for SVA treatment, which helps in achieving higher FF in the later case.

The photoluminescence quenching efficiency (PLQE) is estimated from the PL spectra of pure PTB7-Th and blend films in **Fig. 4b**. A high PLQE value of 86.5% indicates an efficient charge transfer from donor to acceptor. The value of SternVolmer quenching coefficient (K_{sv}) is calculated from the slope of Stern-Volmer plots using the equation $\eta_o/\eta=1+K_{sv}c$, where η and η_o are emission efficiency in presence and absence of quenchers, respectively.¹⁶ A K_{sv} vaue of 9.92×10^4 M⁻¹ is obtained for PTB7-Th:**FRd**₂ blend films (**Fig. S12**), which is higher than reported K_{sv} values for fullerene based acceptors.



Fig. 4 (a) The SCLC fitting of dark IV curves obtained from single carrier devices to estimate the hole and electron mobility of PTB7-Th and FRd_2 , respectively in SVA treated blend films, (b) Photoluminescence quenching spectra.

Atomic force microscopic (AFM) measurement in tapping mode was performed to examine the nanoscale morphology of photoactive layers (**Fig. 5**). The 'thermally annealed' PTB7-Th:**FRd**₂ films show a root mean square (RMS) roughness of 3.8 nm. After SVA treatment, film morphology of PTB7-Th:**FRd**₂ film becomes smoother and the RMS roughness of the film surface is found to be 2.3 nm only. Because of smoother morphology, charge transport and collection is expected to be higher in SVA treated devices, which is in agreement with our device results.



Fig. 5 AFM images of PTB7-Th:FRd₂ blend films treated with (a) thermal annealing and (b) solvent vapor annealing.

The micro-structural features of pure \mathbf{FRd}_2 and blend film prepared under different experimental conditions were studied by two-dimensional grazing-incidence X-ray diffraction (GIXRD). The additive added blend films showed two weak peaks at q~0.14 and 1.7 $\text{\AA}^{\text{-1}}$ due to lamellar (h00) and $\pi\text{--}\pi$ stacking (010), respectively, which marginally improves with SVA treatment as shown in Fig. S13. While it is difficult to draw any conclusion from GIXRD results, the transmission electron microscopy (TEM) images provide more clear information regarding the evolution of PTB7-Th:FRd₂ blend morphology before and after annealing treatments and with or without solvent additive. Fig. 6 shows TEM images of PTB7-Th:FRd2 blend films prepared under different conditions. No distinct feature was found in the 'as cast' as well as 'thermally annealed' blend films without additive. However, addition of DIO additive induces some ordering features, which is most prominent in the case of SVA treated blend films.

COMMUNICATION



Fig. 6 TEM images of PTB7-Th:FRd₂ blend films prepared under different experimental conditions – a) 'as cast' without any additive , b) 'thermally annealed' (w/o additive), c) 'thermally annealed' (DIO additive) and d) 'solvent vapour annealed' (DIO additive).

In conclusion, we have designed and synthesized a new nonfullerene acceptor FRd₂ containing central electron donating fluorene core attached to the rhodanine end groups via benzothiadiazole and furan π -spacer for use in OSCs. **FRd**₂ has good solubility, strong absorption profile ranging from 300 to 620 nm with high molar extinction coefficient, suitable FMO energy levels and good quenching ability. Its photovoltaic performance was studied in inverted structured BHJ OSCs. The PTB7-Th:FRd₂ based OPV devices treated with solvent vapor annealing exibited a highest PCE of 9.4% with a J_{sc} of 15.7 mA/cm² and FF of 72.3%. Deeply lying LUMO energy level of FRd₂ resulted in high V_{oc} of 0.83 V. As PTB7-Th and FRd₂ have absorption profile complementary to each other, both contributed to the photocurrent significantly, which is one of the possible reasons to achieve high PCE. A high EQE value of 75% was also observed in the SVA treated devices. To the best of our knowledge, the PCE of 9.4% is the highest PCE reported ever for fluorene core based fullerene-free OSCs. S. Holliday et al. earlier reported one fluorene core based SMNFA coded as FBR end capped with rhodanine, which demosterated good photovoltaic performance.⁸ We synthesized FRd₂ using same core and chromophroic groups incorporating furan unit to examine the effect of π -spacer on the opto-electronic properties of SMNFA. It is seen that FRd₂ possesses deeper FMO energy levels and lower band gap compared to FBR. Hence, Introduction of furan π -spacer appears to be a good strategy to develop efficient SMNFAs by extending π conjugation through molecular backbone. This work demostrates that fluorene based SMNFAs have potential to achieve high PCE by suitable molecular engineering and proper optimization of device fabrication steps.

The authors gratefully acknowledge the financial support of Indo-UK APEX project (Phase-II). Suman thanks UGC for providing SRF. AB would like to thank DST for Inspire Faculty fellowship DST/INSPIRE/04/2017/000087.

REFERENCES

Published on 06 November 2017. Downloaded by Northwestern University on 07/11/2017 01:05:15.

 (a) Y. Zhou, L. Ding, K. Shi, Y. Z. Dai, N. Ai, J. Wang and J. Pei, *Adv. Mater.*, 2012, **24**, 957; (b) K. Cnops, B. P. Rand, D. Cheyns, B. Verreet, M. A. Empl and P. Heremans, *Nat. Commun.*, 2014, **5**, 3406.

- (a) F. Zhao, S. Dai, Y. Wu, Q. Zhang, J. Wang, L. Jiang, Q. Ling, Z. Wei, W. Ma, W. You, C. Wang and X. Zhan, *Adv. Mater.*, 2017, **29**, 1700144; (b) W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang and J. Hou, *J. Am. Chem. Soc.*, 2017, **139**, 7148.
- (a) Z. Jiang, Z. Liu, C. Yang, C. Zhong, J. Qin, G. Yu and Y. Liu, *Adv. Funct. Mater.*, 2009, **19**, 3987; (b) S. H. Lee and T. Tsutsui, *Thin Solid Films*, 2000, **363**, 76.
- (a) F. Huang, K.-S. Chen, H.-L. Yip, S. K. Hau, O. Acton, Y. Zhang, J. Luo and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2009, 131, 13886; (b) C.-H. Lee, Y.-Y. Lai, F.-Y. Cao, J.-Y. Hsu, Z.-L. Lin, U. S. Jeng, C.-J. Su and Y.-J. Cheng, *J. Mater. Chem. C*, 2016, 4, 11427; (c) Z. Liu, W. Li, S. Topa, X. Xu, X. Zeng, Z. Zhao, M. Wang, W. Chen, F. Wang, Y.-B. Cheng and H. He, *ACS Appl. Mater. Interfaces*, 2014, 6, 10614; (d) Z. Liu, D. Xiong, X. Xu, Q. Arooj, H. Wang, L. Yin, W. Li, H. Wu, Z. Zhao, W. Chen, M. Wang, F. Wang, Y.-B. Cheng and H. He, *ACS Appl. Mater. Interfaces*, 2014, 6, 3448; (e) E. Zhou, K. Hashimoto and K. Tajima, *Polymer*, 2013, 54, 6501.
- (a) C. Liu, L. Zhang, L. Xiao, X. Peng and Y. Cao, ACS Appl. Mater. Interfaces, 2016, 8, 28225; (b) Q. Zheng, B. J. Jung, J. Sun and H. E. Katz, J. Am. Chem. Soc., 2010, 132, 5394.
- 6. Y.-C. Hung, J.-C. Jiang, C.-Y. Chao, W.-F. Su and S.-T. Lin, *J. Phys. Chem. B*, 2009, **113**, 8268.
- (a) P. Qin, X. Yang, R. Chen, L. Sun, T. Marinado, T. Edvinsson, G. Boschloo and A. Hagfeldt, *J. Phys. Chem. C*, 2007, **111**, 1853; (b) D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt and L. Sun, *J. Org. Chem.*, 2007, **72**, 9550.
- (a) Suman, A. Bagui, V. Gupta, K. K. Maurya and S. P. Singh, J. Phys. Chem. C, 2016, 120, 24615; (b) Suman, V. Gupta, A. Bagui and S. P. Singh, Adv. Funct. Mater., 2016, 1603820; (c) S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson and I. McCulloch, J. Am. Chem. Soc., 2015, 137, 898; (d) K. Wang, Y. Firdaus, M. Babics, F. Cruciani, Q. Saleem, A. El Labban, M. A. Alamoudi, T. Marszalek, W. Pisula, F. Laquai and P. M. Beaujuge, Chem. Mater., 2016, 28, 2200.
- P. E. Schwenn, K. Gui, A. M. Nardes, K. B. Krueger, K. H. Lee, K. Mutkins, H. Rubinstein-Dunlop, P. E. Shaw, N. Kopidakis, P. L. Burn and P. Meredith, *Advanced Energy Materials*, 2011, 1, 73.
- Y. Wu, H. Bai, Z. Wang, P. Cheng, S. Zhu, Y. Wang, W. Ma and X. Zhan, *Energy Environ Sci.*, 2015, 8, 3215.
- B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni, G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang, Y. Cao, T. P. Russell and Y. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 3886.
- S. Li, W. Liu, M. Shi, J. Mai, T.-K. Lau, J. Wan, X. Lu, C.-Z. Li and H. Chen, *Energy Environ Sci.*, 2016, 9, 604.
- Y. Lin, Z.-G. Zhang, H. Bai, J. Wang, Y. Yao, Y. Li, D. Zhu and X. Zhan, *Energy Environ Sci.*, 2015, **8**, 610.
- H. Lin, S. Chen, H. Hu, L. Zhang, T. Ma, J. Y. L. Lai, Z. Li, A. Qin, X. Huang, B. Tang and H. Yan, *Adv. Mater.*, 2016, 28, 8546.
- 15. R. W. G. N. F. Mott, *Electronic Processes in Ionic Crystals*, Oxford University Press, Oxford, 1940.
- O. Y. Park, H. U. Kim, J.-H. Kim, J. B. Park, J. Kwak, W. S. Shin, S. C. Yoon and D.-H. Hwang, *Sol. Energy Mater Sol. Cells*, 2013, **116**, 275.