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Indolo[3,2-*b*]indole donor-based D- π -A dyes for DSCs: investigating the role of π -spacers towards recombination†

P. V. Santhini,^{‡ab} Jayadev V.,^{‡bc} Sourava C. Pradhan,^{bc} Sivasankaran Lingamoorthy,^{bc} Nitha P. R.,^{ab} Chaithanya M. V.,^a Rakesh K. Mishra,^d Narayanan Unni K. N.,^{ID *bce} Jubi John^{ID *ab} and Suraj Soman^{ID *bce}

Dye solar cells (DSCs) are gaining increasing interest since the recent realization of their high-performance potential in low/indoor light environments. Fused conjugated metal-free organic dyes have become a prominent class of dyes used in DSC in recent times by virtue of their better backbone rigidity, efficient charge transport properties, and the opportunity they provide for further structural modifications. Herein, we report the synthesis and characterization of three metal-free D- π -A organic dyes employing indolo[3,2-*b*]indole as the donor unit. The optical, electrochemical and photovoltaic properties have been analyzed in detail as a function of π -spacers, namely, benzene (**IID-1**), thiophene (**IID-2**) and furan (**IID-3**). Eventually, the best performance was demonstrated by the dye bearing benzene as the π -spacer. The role of recombination in determining the photovoltaic performance as a function of the nature of π -spacers was explored in detail, using various perturbation techniques on the fabricated devices, and compared with the results obtained from molecular orbital calculations.

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1. Introduction

The increasing energy demand worldwide is as a result of the growing human population and necessitates the need to investigate new sustainable energy sources that are capable of reducing the growing consumption of fossil fuels. Of the existing renewable energy technologies, photovoltaics (PV) occupy a prominent position.¹ Among the various third generation photovoltaic technologies, DSCs represent a unique, emerging area of PV research that has been gaining widespread interest among research communities in recent years based on

their ease of fabrication, relatively low cost, flexibility of integration into a range of substrates, colour tunability, transparency and, above all, the ability to harness indoor/diffused light and to convert it into useful power with very high efficiencies as compared to silicon and thin film technologies.^{2,3} Recently, Michael Grätzel and Anders Hagfeldt reported power conversion efficiencies above 30% in indoor light harvesting conditions, which resulted in a paradigm shift in this area of photovoltaic research.^{4,5}

In DSC, the dye plays the major role in harnessing the light. Conventionally, Ru complexes, Zn porphyrins, and metal-free organic dyes used to serve as the most promising candidates in DSCs.^{6–13,63,64} Even though Ru-based sensitizers have been proved to be highly efficient and stable, they lack the opportunity for higher structural modifications in addition to the scarcity of Ru metal, which has resulted in the introduction of stable organic dyes that can be easily synthesized, having higher molar extinction coefficients, lower cost and low toxicity.^{7,14} Metal-free organic sensitizers are compatible with alternative redox electrolytes like cobalt and copper, achieving impressive power conversion efficiencies of 12–15% and higher voltages (>1 V from a single junction device) in full sun conditions.^{15–20} Organic metal-free dyes have been made in different architectures such as D- π -A, D-A- π -A and D-D- π -A, featuring improved performance.^{21–25}

Thiophene and furan spacers have successfully showcased improved current density, leading to superior photovoltaic

^a Organic Chemistry Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, 695019, India. E-mail: jubijohn@niist.res.in

^b Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST Campus, Thiruvananthapuram 695019, India

^c Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram 695019, India. E-mail: unni@niist.res.in, suraj@niist.res.in

^d Department of Sciences and Humanities, National Institute of Technology, Uttarakhand (NITUK), Srinagar (Garhwal) 246174, India

^e CSIR-Network of Institutes for Solar Energy (CSIR-NISE), India

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‡ Both authors contributed equally to this work.

performance in comparison to benzene when employed as π -spacers in metal-free organic dyes having the D- π -A architecture. This is attributed to the smaller resonance energy of thiophene and lower aromatic energy of furan, which results in enhanced conjugation, optical properties, and better charge carrier mobilities in comparison to dyes using benzene as π -spacer.^{26–28} Recently, Graeme Cooke and co-workers have demonstrated improvement in current density and efficiency by swapping thiophene with a furan spacer in D- π -A porphyrin dyes.²⁹ Similarly, Hou and co-workers observed the same trend in performance on changing the spacer from benzene to thiophene, employing a similar kind of fused aromatic indeno[1,2-*b*]indole as the donor unit.³⁰ Bhanuprakash and co-workers have also shown an increase in current density (J_{sc}) and efficiency (η) on changing spacers from benzene to thiophene to furan, employing benzocarbazole as the donor and cyanoacrylic acid as the acceptor.³¹ A similar behavior has also been reported by Lin and co-workers on employing a D-A- π -A architecture.³²

Herein, we report the successful synthesis and characterization of three metal-free D- π -A organic dyes (**IID-1**, **IID-2**, and **IID-3**), where we have incorporated a fused ring N-hetero aromatic indolo[3,2-*b*]indole donor functionality as shown in Scheme 1. Indoloindoles are an interesting class of N-heteroacenes of which indolo[3,2-*b*]indoles are considered to be good electron donors.³³ This donor character of the indolo[3,2-*b*]indole moiety can be attributed to the small atomic radius of the N-atom, which in turn results in a more dense assembly of molecules. In addition, these molecules are also known to possess better charge carrier mobility due to the bidirectional electronic coupling enabled by NH- π interactions.^{34,35} These fused N-heteroacenes have been used in the development of organic photovoltaics, organic field-effect transistors, heterojunction solar cells and high-spin organic polymers.^{36–41} However, the lack of competent synthetic routes in making indolo[3,2-*b*]indoles has limited its widespread material applications.^{38,42–48} Very recently, we introduced a facile route involving a sequential MCR-oxidation approach to the synthesis of these fused indole heteroacenes.^{49,50} The present methodology involves an initial MCR of an enolizable ketone (cyclohexanone), a 1° amine, and *N*-tosyl-3-nitroindole furnishing the intermediate pyrrolo[3,2-*b*]indole, which on further oxidation with chloranil affords indolo[3,2-*b*]indole moieties in good yields. The advantage of our method as compared existing methods was clearly demonstrated by the generation of symmetrical and unsymmetrical indolo[3,2-*b*]indoles, which are highly relevant for material applications.^{49,50}

Scheme 1 Chemical structure of the indolo[3,2-*b*]indole dyes.

The strategically synthesized indolo[3,2-*b*]indole dyes (**IID** series) were found to offer many promising features, considering the functionalities that are required for a stable and efficient DSC dye, which include (1) extended π -conjugation that enhances the intermolecular interaction; (2) a symmetric conjugated structure leading to a more rigid backbone; (3) properly placed alkyl groups for increased solubility, to prevent the approach of triiodide in getting closer to TiO_2 and also to prevent aggregation. These interesting skeletal characteristics make indolo[3,2-*b*]indole a potential building block for use in DSC. Recently, Nopporn and co-workers also showed the potential of this nitrogen-bridged phenylenevinylene unit to be used in DSCs.⁶² Our focus was to explore its potential as a donor in a D- π -A dye architecture and to study in detail how the variation in π -spacers linking the indolo[3,2-*b*]indole donor to the cyanoacrylic acid acceptor affects the physical properties and in particular, the PV performance. Unlike the previous reports on D- π -A dyes that showed improved current density and photovoltaic performance employing conjugated thiophene and furan heterocyclic spacers, in the present work, incorporating these π -linker groups led to more recombination and lower lifetimes, resulting in lower PV performance. The enhanced performance of the benzene-substituted dye, **IID-1**, is attributed to reduced interception (recombination), which was studied in detail using open-circuit voltage decay (OCVD), intensity modulated photovoltage spectroscopy (IMVS) and electrochemical impedance spectroscopy (EIS) measurements and was correlated to the structural properties of dyes obtained from detailed theoretical calculations.

2. Experimental

2.1 General methods

All chemicals were of the best grade commercially available and were used without further purification. The 1-*tert*-butyl-3-nitroindoles were prepared by following the literature report.⁵¹ All solvents were purified according to the standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulphate binder. Gravity column chromatography was performed using neutral alumina and mixtures of hexane-ethyl acetate were used for elution.

Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker AMX 500 spectrophotometer (with CDCl_3 and acetone- d_6 as solvents). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signals of chloroform- d (δ 7.25 ppm) and acetone- d_6 (2.05 ppm). Multiplicities were given as follows: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplet). Coupling constants are reported as J values in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signals of

chloroform- d (δ 77.03 ppm) acetone- d_6 (29.84 and 206.26 ppm). In some of the cases, the ^{13}C spectra of compounds were recorded in a 7:3 mixture of CDCl_3 and CCl_4 . In those ^{13}C spectra, a peak is seen at δ 96.0 ppm, which corresponds to the carbon of CCl_4 . Mass spectra were recorded under ESI/HRMS at 60 000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on a Bruker FT-IR spectrometer.

2.2 Device fabrication and characterization

The FTO (working electrodes, GreatCell Solar) were cleaned and heated to 500 °C, followed by UV- O_3 cleaning. Then, the pre-blocking layer was coated by immersing the cleaned electrodes in 40 mM TiCl_4 solution at 70 °C for 30 min. By the doctor-blading technique, 16 μm of TiO_2 (GreatCell Solar) (12 μm transparent 18 NR-T layer and 4 μm scattering 18 NR-AO layer) was coated on the working electrodes, then through ramping, the working electrodes were heated to 500 °C. The TiO_2 coated electrodes were then soaked for 15 h in 0.2 mM dye solutions with 20 mM chenodeoxycholic acid (CDCA) in methanol at room temperature. The Pt paste (GreatCell Solar) was coated on the cleaned counter electrode substrates having pre-drilled holes and were annealed at 380 °C for 20 minutes. The cells were assembled using Surlyn (25 μm) spacer and filled with standard I^-/I_3^- electrolyte.

The J - V characteristics were measured under AM 1.5G one sun irradiation, 100 mW cm^{-2} using a Newport Class AAA solar simulator, Sol3A-94023. The incident-photon-to-current conversion efficiency (IPCE) was measured using a 350 W xenon lamp in dc mode (Newport). The open-circuit voltage decay (OCVD), intensity modulated photo-voltage spectroscopy (IMVS) and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical workstation (Autolab PGSTAT 302N). The photo-voltage responses were measured using LED, with a frequency range varying from 0.1 Hz to 10 kHz using a 10% dc light perturbation. EIS was performed in the dark employing a frequency range from of 100 kHz to 0.1 Hz.

2.3 Synthesis of dyes

2.3.1 General procedure for the synthesis of indolo[3,2-*b*]-indole. The enolizable ketone, cyclohexanone (2.0 equiv.), and primary amine, *n*-hexylamine (2.0 equiv.), were weighed into a dry reaction tube. Dry toluene along with 4 Å MS (50 mg) was added and allowed to stir at 60 °C for 1 hour, after which 3-nitro-*N*-tosyl indole (1.0 equiv.) was added and it was kept stirring at the same temperature for 11 hours. After the complete consumption of 3-nitro-*N*-tosyl indole, chloranil (3.0 equiv.) was added along with toluene and kept at 100 °C for 10 hours. The solvent was evaporated *in vacuo* and the residue on activated neutral alumina column chromatography yielded indolo[3,2-*b*]-indole with hexanes and ethyl acetate as eluent.

tert-Butyl 8-bromo-10-hexylindolo[3,2-*b*]indole-5(10*H*)-carboxylate (**4**). The reaction was performed according to general procedure with 5-bromo-3-nitro-*N*-Boc indole (500 mg, 1.47 mmol), *n*-hexylamine (297 mg, 2.94 mmol), cyclohexanone (288 mg, 2.94 mmol)

and chloranil (1084 mg, 4.41 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (483 mg, 70%). TLC (SiO_2): R_f 0.71 (7% ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3 , TMS): δ 8.44–8.43 (m, 1H), 8.14–8.13 (m, 1H), 7.78 (s, 1H), 7.41–7.35 (m, 2H), 7.29–7.24 (m, 1H), 7.16 (t, J = 8 Hz, 1H), 4.38 (t, J = 8 Hz, 2H), 1.92–1.86 (m, 2H), 1.79 (s, 9H), 1.38–1.25 (m, 6H), 0.85 (t, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.4, 140.7, 126.9, 126.5, 122.9, 121.9, 120.4, 119.9, 119.2, 118.3, 116.0, 115.8, 109.5, 84.3, 44.9, 31.6, 30.3, 28.6, 26.7, 22.5, 14.0; HRMS (ESI-Orbitrap) m/z : ($\text{M} + \text{Na}$) $^+$ calcd for $\text{C}_{25}\text{H}_{29}\text{BrN}_2\text{O}_2\text{Na}$: 491.1305; found: 491.1320.

3-Bromo-5-ethyl-5,10-dihydroindolo[3,2-*b*]indole (**5**). To a stirred solution of **4** (400 mg, 0.85 mmol) in DCM (15 mL), TFA (10%) was added portion-wise under nitrogen atmosphere at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 3 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and water was added, followed by extraction with EtOAc. The organic layer was washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the deprotected compound **5** as a white solid (282 mg, 90%). m.p. 145–148 °C; ^1H NMR (500 MHz, acetone): δ 10.42 (s, 1H), 7.90 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.17–7.16 (m, 1H), 7.14–7.11 (m, 1H), 6.97–6.94 (m, 1H), 4.43 (t, J = 7.0 Hz, 2H), 1.81–1.75 (m, 2H), 1.28–1.23 (m, 2H), 1.18–1.02 (m, 4H), 0.67 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, acetone): δ 141.1, 139.4, 126.1, 125.6, 124.0, 122.3, 119.7, 118.1, 116.4, 114.4, 113.8, 110.8, 110.0, 44.7, 31.4, 30.2, 29.4, 29.3, 29.1, 29.0, 28.8, 28.7, 28.5, 26.4, 22.3, 13.4; HRMS (ESI-Orbitrap) m/z : ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Br}$: 369.0961; found: 369.0972.

3-Bromo-5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole (**6**). To a stirred solution of **5** (250 mg, 0.68 mmol) in a mixture of THF:DMF (8:2, 5 mL), NaH (41 mg, 1.62 mmol) was added portion-wise under nitrogen atmosphere at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled again to 0 °C and 1-bromohexane (134.7 mg, 0.82 mmol) was added dropwise and stirred at room temperature for 8 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and water was added, and then extracted with EtOAc. The organic layer was washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure; the residue on activated neutral alumina column chromatography (2% ethyl acetate in hexane) yielded compound **6** as a white solid (252 mg, 82%). m.p. 70 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.34–7.25 (m, 3H), 7.15 (t, J = 7.5 Hz, 1H), 4.46–4.43 (m, 4H), 1.98–1.92 (m, 4H), 1.41–1.30 (m, 4H), 1.27–1.25 (m, 8H), 0.87–0.83 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 140.9, 139.0, 124.0, 122.2, 120.0, 118.2, 117.8, 114.3, 110.9, 109.8, 45.3, 31.6, 30.2, 26.8, 22.5, 14.0; HRMS (ESI-Orbitrap) m/z : ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{Br}$: 453.1900; found: 453.1907.

4-(5,10-Diethyl-5,10-dihydroindolo[3,2-b]indol-3-yl) benzaldehyde (7). A mixture of indoloindole **6** (250 mg, 0.551 mmol), 4-formyl phenyl boronic acid (124 mg, 0.83 mmol), Pd(PPh₃)₄ (64 mg, 0.055 mmol), and K₂CO₃ (380 mg, 2.75 mmol) was weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF (5 mL) and water (1.5 mL) were added, then the reaction mixture was purged with argon and allowed to stir at 65 °C for 24 hours. The solvent was evaporated in vacuum and the residue on activated neutral alumina column chromatography (3% ethyl acetate in hexane) yielded the product as a white amorphous solid (171 mg, 65%). TLC (SiO₂): R_f 0.38 (7% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ 10.07 (s, 1H), 8.08–8.04 (m, 1H), 7.98 (d, *J* = 8 Hz, 2H), 7.87 (d, *J* = 8 Hz, 2H), 7.58–7.53 (m, 2H), 7.50–7.42 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.54–4.52 (m, 4H), 2.03–1.99 (m, 4H), 1.46–1.43 (m, 4H), 1.35–1.25 (m, 8H), 0.87–0.83 (m, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 192.0, 148.7, 140.7, 140.5, 134.4, 130.4, 129.6, 127.6, 122.0, 121.1, 118.3, 117.8, 116.6, 115.2, 110.2, 109.9, 45.5, 45.4, 31.6, 30.3, 29.7, 26.8, 22.6, 14.0; HRMS (ESI-Orbitrap) *m/z*: (M + H)⁺ calcd for C₃₃H₃₉N₂O: 479.3057; found: 479.3043.

(E)-2-Cyano-3-(4-(5,10-dihexyl-5,10-dihydroindolo[3,2-b] indol-3-yl)phenyl)acrylic acid (IID-1). A mixture of aldehyde **7** (150 mg, 0.31 mmol), cyanoacetic acid (80 mg, 0.94 mmol), ammonium acetate (119 mg, 1.55 mmol) in acetic acid (3.0 mL) was heated at reflux overnight under an argon atmosphere. After cooling to room temperature, it was precipitated by pouring into water. The precipitate was washed with water and dried in a vacuum oven. The product was obtained as a red solid (130 mg, 77%). m.p. 180–183 °C; ¹H NMR (500 MHz, acetone) δ 8.38 (s, 2H), 8.23 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.71 (t, *J* = 7.0 Hz, 2H), 4.65 (t, *J* = 7.0 Hz, 2H), 2.05–1.98 (m, 4H), 1.45–1.42 (m, 4H), 1.36–1.23 (m, 8H), 0.84–0.79 (m, 6H); ¹³C NMR (125 MHz, acetone) δ 162.4, 153.7, 146.6, 145.6, 140.4, 140.3, 131.2, 129.1, 128.8, 126.8, 126.0, 125.3, 121.4, 120.3, 117.7, 117.3, 116.1, 115.4, 114.8, 114.0, 110.1, 109.6, 103.8, 101.3, 44.4, 44.2, 30.9, 30.9, 29.6, 28.9, 26.0, 21.8, 21.8, 12.8, 12.8; HRMS (ESI-Orbitrap) *m/z*: (M)⁺ calcd for C₃₆H₃₉N₃O₂: 545.3037; found: 545.3033.

5-(5,10-Dihexyl-5,10-dihydroindolo[3,2-b]indol-3-yl) thiophene-2-carbaldehyde (8). A mixture of indoloindole **6** (250 mg, 0.551 mmol), (5-formylthiophene-2-yl)boronic acid (129 mg, 0.83 mmol), Pd(PPh₃)₄ (64 mg, 0.055 mmol), K₂CO₃ (380 mg, 2.75 mmol) was weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF (5 mL) and water (1.5 mL) were added, then the reaction mixture was purged with argon and allowed to stir at 65 °C for 24 hours. The solvent was evaporated under vacuum and the residue on activated neutral alumina column chromatography (3% ethyl acetate in hexane) yielded the product as a white amorphous solid (160 mg, 60%). TLC (SiO₂): R_f 0.39 (7% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 1H), 8.13 (s, 1H), 7.84 (d, *J* = 7 Hz, 1H), 7.77–7.76 (m, 1H), 7.62–7.60 (m, 1H), 7.49–7.47 (m, 2H), 7.43–7.42 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.53–4.49

(m, 4H), 2.00–1.99 (m, 4H), 1.48–1.42 (m, 4H), 1.34–1.26 (m, 8H), 0.86–0.84 (m, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 182.6, 157.0, 141.1, 140.8, 137.9, 127.0, 125.8, 123.3, 122.7, 122.2, 120.1, 118.4, 117.8, 116.0, 115.0, 114.4, 110.2, 109.9, 45.6, 45.4, 31.6, 31.6, 30.3, 30.2, 26.9, 26.8, 22.6, 22.5; HRMS (ESI-Orbitrap) *m/z*: (M + H)⁺ calcd for C₃₁H₃₇N₂O: 485.2621; found: 485.2634.

(E)-2-Cyano-3-(5-(5,10-dihexyl-5,10-dihydroindolo[3,2-b] indol-3-yl)thiophen-2-yl) acrylic acid (IID-2). A mixture of aldehyde **8** (150 mg, 0.31 mmol), cyanoacetic acid (80 mg, 0.94 mmol), ammonium acetate (119 mg, 1.55 mmol) in acetic acid (3.0 mL) was heated at reflux overnight under an argon atmosphere. After cooling to room temperature, it was precipitated by pouring into water. The precipitate was washed with water and dried in a vacuum oven. The product was obtained as a red solid (108 mg, 63%). M.p. 240–242 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.30 (s, 1H), 8.13–8.07 (m, 1H), 7.83–7.75 (m, 2H), 7.70–7.66 (m, 1H), 7.61–7.59 (m, 1H), 7.49–7.47 (m, 1H), 7.45–7.42 (m, 1H), 7.35–7.32 (m, 1H), 7.20 (t, *J* = 7.5 Hz) 4.51 (t, *J* = 7 Hz, 2H), 4.47 (t, *J* = 7 Hz, 2H), 2.01–1.97 (m, 4H), 1.46–1.40 (m, 4H), 1.31–1.25 (m, 8H), 0.87–0.82 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 158.7, 147.7, 141.0, 140.9, 140.2, 139.5, 133.5, 129.3, 126.6, 123.3, 123.0, 122.3, 120.5, 118.5, 117.9, 116.1, 110.4, 110.0, 45.6, 31.6, 30.3, 30.2, 29.7, 26.8, 26.8, 22.5, 14.0; HRMS (ESI-Orbitrap) *m/z*: (M)⁺ calcd for C₃₄H₃₇N₃O₂S: 551.2601; found: 551.2610.

5-(5,10-Dihexyl-5,10-dihydroindolo[3,2-b]indol-3-yl)furan-2-carbaldehyde (9). A mixture of indoloindole **6** (250 mg, 0.551 mmol), (5-formylfuran-2-yl)boronic acid (116 mg, 0.83 mmol), Pd(PPh₃)₄ (64 mg, 0.055 mmol), K₂CO₃ (380 mg, 2.75 mmol) was weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF (5 mL) and water (1.5 mL) were then added and the reaction mixture was purged with argon and allowed to stir at 65 °C for 24 hours. The solvent was evaporated under vacuum and the residue on activated neutral alumina column chromatography (3% ethyl acetate in hexane) yielded the product as a white amorphous solid (170 mg, 66%). TLC (SiO₂): R_f 0.37 (7% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ 9.63 (s, 1H), 8.29 (s, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.50–7.46 (m, 2H), 7.36 (d, *J* = 3.5 Hz, 1H), 7.31 (t, *J* = 8 Hz, 1H), 7.21–7.18 (m, 1H), 6.82 (d, *J* = 4 Hz, 1H), 4.54 (t, *J* = 7 Hz, 2H), 4.49 (t, *J* = 7.5 Hz, 2H), 2.00–1.97 (m, 4H), 1.46–1.43 (m, 4H), 1.34–1.25 (m, 8H), 0.84–0.82 (m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 161.8, 151.5, 149.8, 144.9, 140.9, 140.8, 129.2, 128.1, 126.8, 125.9, 125.3, 123.2, 122.1, 119.3, 118.4, 117.8, 115.9, 115.2, 114.8, 114.4, 112.6, 110.1, 110.0, 106.0, 45.5, 45.4, 31.6, 31.5, 30.9, 30.4, 30.2, 29.7, 26.8, 22.5, 14.0; HRMS (ESI-Orbitrap) *m/z*: (M + H)⁺ calcd for C₃₁H₃₇N₂O₂: 469.2850; found: 469.2863.

(E)-2-Cyano-3-(5-(5,10-dihexyl-5,10-dihydroindolo[3,2-b] indol-3-yl)furan-2-yl) acrylic acid (IID-3). A mixture of aldehyde **9** (150 mg, 0.32 mmol), cyanoacetic acid (82 mg, 0.96 mmol), ammonium acetate (123 mg, 1.6 mmol) in acetic acid (3.0 mL) was heated at reflux for overnight under argon atmosphere. After cooling to room temperature, it was precipitated by pouring into water.

The precipitate was washed with water and dried in a vacuum oven. The product was obtained as a red solid (120 mg, 70%). M.p. 190–193 °C; ^1H NMR (500 MHz, acetone): δ 8.73 (s, 1H), 8.09 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 3.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 4.71–4.67 (m, 4H), 2.03–1.97 (m, 4H), 1.49–1.43 (m, 4H), 1.36–1.21 (m, 8H), 0.85–0.79 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 163.8, 162.2, 147.4, 141.0, 137.5, 127.1, 121.9, 119.0, 118.5, 116.5, 110.7, 110.4, 107.5, 95.1, 44.9, 31.5, 31.4, 26.4, 26.2, 22.3, 13.3, 13.3; HRMS (ESI-Orbitrap) m/z : $(\text{M} + \text{H})^+$ calcd for $\text{C}_{34}\text{H}_{37}\text{N}_3\text{O}_3$: 535.2829; found: 535.2820.

3. Results and discussion

3.1 Synthesis and characterization

The synthesis of indolo[3,2-*b*]indole-based dyes following the D- π -A approach commenced with the one-pot MCR/oxidation of *N*-Boc-5-bromo-3-nitro-indole **1**, cyclohexanone **2** and hexylamine **3**. The Boc-group on the indoloindole **4** was easily removed by treatment with trifluoroacetic acid in DCM, furnishing the intermediate **5** in 90% yield. This fused indole moiety **5** was then subjected to *N*-alkylation with hexylbromide to afford the donor dihexylindoloindole **6** in excellent yield. The π -spacer was attached to the donor moiety by Suzuki reaction of **6** with formyl-aryl/heteroaryl boronic acids such as 4-formyl phenyl boronic acid, (5-formylthiophen-2-yl)boronic acid and (5-formylfuran-2-yl)boronic acid to afford the molecules **7**, **8** and **9**, respectively. Finally, the acceptor part was attached to **7**, **8** and

9 via Knoevenagel condensation with cyanoacetic acid furnishing the dyes **IID-1**, **IID-2**, and **IID-3**, respectively. The entire synthetic route is shown in Scheme 2.

3.2 Optical and electrochemical properties

The absorption spectra for all three dyes were recorded in dichloromethane solvent and are shown in Fig. 1(a). Benefiting from the D- π -A architecture, all of the above sensitizers (**IID-1**, **IID-2**, and **IID-3**) exhibited absorption in the range of 300–600 nm. The bands observed at shorter wavelengths correspond to π - π^* transitions and the ones at longer wavelengths are attributed to intra-molecular charge transfer (ICT) transitions. All three dyes can be clearly distinguished by analyzing their characteristic intra-molecular charge transfer band. The dyes **IID-1**, **IID-2**, and **IID-3** displayed absorption maxima at 357 nm, 385 nm and 447 nm, respectively. The variation in absorption spectra is attributed to the presence of different π -spacers and the dihedral angle between the indolo[3,2-*b*]donor and the π -spacers, which play a key role in determining the absorption maxima and shift in absorption spectra. The hetero-atomic π -spacers like thiophene and furan in **IID-2** and **IID-3** decreased the energy band gap of these dyes, which resulted in a bathochromic as well as a hyperchromic shift in absorption spectra as compared to the non-heteroatomic π -spacer, *i.e.* benzene present in **IID-1**. Both dyes **IID-2** and **IID-3** showed a red-shifted absorption and higher molar extinction coefficient in comparison to **IID-1**.

To investigate in detail the feasibility of electron injection from the excited state of the dye to the semiconductor (TiO_2) conduction band (CB) and regeneration of the oxidized ground

Scheme 2 Synthetic route adopted for indolo[3,2-*b*]indole-based dyes **IID-1**, **IID-2** and **IID-3**.

Fig. 1 (a) Absorption spectra of IID-1, IID-2, and IID-3 measured in dichloromethane. (b) Cyclic voltammogram of the IID-1, IID-2, and IID-3 dyes in methanol solution using F_c/F_c^+ as internal reference.

state of the dye by the electrolyte, cyclic voltammetry was used to study the electrochemical properties of the sensitizers (Fig. 1(b)). Cyclic voltammetry was performed for all three dyes, employing methanol as the solvent in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard; micro surface gold was used as the anode, platinum wire as the cathode and Ag/AgCl as the reference electrode. The oxidation potentials of IID-1, IID-2, and IID-3 were calculated with respect to ferrocene and were converted to NHE using the equation, $E_{HOMO} = [E_{ox} + 0.66 \text{ V}]$. The LUMO of these dyes were calculated by taking the difference between the E_{HOMO} and E_{0-0} band gap of the dyes obtained from the intersection of the absorption and emission spectra. All photophysical and electrochemical values are tabulated in Table 1. The first redox potentials for IID-1, IID-2, and IID-3 were 0.92 V, 0.95 V and 0.92 V vs. NHE, respectively which are at more positive potentials in comparison to the iodide/triiodide redox system (0.4 V vs. NHE). The excited state potential of the dyes were estimated to be -1.99 V , -1.98 V and -1.48 V , which are more negative than the TiO_2 conduction band energy level (-0.5 V vs. NHE), affirming smooth electron injection from the dye excited states for all three dyes. Schematic representations of the energy-level diagrams of sensitizers, electrolyte, and TiO_2 are given in Fig. 2.

Table 1 Photophysical and electrochemical data of IID dyes

Sensitizers	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) ^a	E_{ox}^b (Ag/AgCl) eV	HOMO (vs. NHE)	E_{0-0}^c eV	LUMO (vs. NHE)
IID-1	357 (20 620)	0.259	0.92	2.91	-1.99
IID-2	385 (32 960)	0.291	0.95	2.89	-1.98
IID-3	447 (35 703)	0.259	0.92	2.39	-1.48

^a Absorption spectra for all the dyes were recorded at $4 \times 10^{-5} \text{ M}$ concentration. ^b Oxidation potentials for all dyes were recorded at 1 mM concentration. ^c Calculated from the intersection of absorption and emission spectra in the same solvent.

Fig. 2 Energy level diagram of IID dyes, TiO_2 and electrolyte.

3.3 Molecular geometry and orbital calculation of the dyes

The ability of dyes to exhibit better photovoltaic properties predominantly rely on their photophysical, electrochemical and detailed pre-experimental information on the molecular geometry, electron density distribution and spectroscopic properties. Adept knowledge of the above-mentioned parameters will help us to understand the electron transfer in more detail, which in turn acts as a useful tool for further modifications to improve the performance. In addition, the degree of π -conjugation, which determines how efficiently the donor-acceptor interactions take place in these molecular systems, is judged by the dihedral angle between the donor, π -spacer and terminal acceptor groups.^{52,53} Keeping this in mind, geometrical optimizations in the gas phase were carried out for all three IID dyes under study. The density functional theory (DFT) calculation was performed at the B3LYP exchange-correlation functional level of theory with the 6-311g(d,p) basis set using a Gaussian G09 package.⁵⁴⁻⁵⁶ All the optimized structures were subjected to vibrational analysis to check for imaginary frequencies. Gaussview 5.0 was used for the visualization of structures and has been given in Fig. 3.⁵⁷ In the π -conjugated system, analogous to IID dyes having D- π -A architecture, charge transport occurs between the donor and the terminal acceptor *via* π -spacer units and is directly dependent on the corresponding dihedral angles (Fig. 3). It is quite clear from Fig. 3, that the introduction of different spacers into D- π -A type IID systems lead to a different twist between the

Fig. 3 Energy minimized structures of IID dyes and the corresponding dihedral angles between the indolo[3,2-*b*]indole donor and the neighboring fragments.

indolo[3,2-*b*]indole donor unit and the π -spacer. The dihedral angle between the indolo[3,2-*b*]indole donor and the phenyl unit in **IID-1** was calculated to be around 34.48° , while in the case of thiophene (**IID-2**), a dihedral angle of 21.99° was obtained. On the other hand, for **IID-3**, indolo[3,2-*b*]indole-furan moieties are more or less aligned in the same plane and the dihedral angle was found to be 1.66° . The terminal cyanoacrylic acid was found to be almost coplanar with respective π -conjugated spacers, displaying dihedral angles between 0.48 – 2.22° .

The large dihedral angle of twist between the donor and π -spacer can possibly help with a more effective blockage of the approach of the oxidized species present in the electrolyte to TiO_2 , thereby leading to a lower recombination for the system having a higher molecular twist. In the present case, the dihedral angle between the donor and π -spacer increases in the order **IID-3** (1.66°) < **IID-2** (21.99°) < **IID-1** (34.48°). **IID-1**, with a comparatively higher twist, should prevent more of the recombination in comparison to **IID-2** and **IID-3**, which holds true based on the lifetime measurements discussed in the photovoltaic section. At the same time, an increased dihedral angle retards the electronic communication between the donor

and acceptor, which led to a blue-shifted absorption and lower absorption coefficient for **IID-1** in comparison to **IID-2** and **IID-3** as given in Fig. 1(a) and Table 1. The alkyl substituents grafted onto the indolo[3,2-*b*]indole donor do not appear to affect the planarity of the dye molecules.

To simulate experimental UV/Vis spectra of the dyes, these optimized geometries were subjected to single-point time-dependent DFT (TDDFT) calculations. The isodensity plots of frontier molecular orbitals and the energy levels of the IID dyes are depicted in Fig. 4. The HOMO of all IID dyes are largely localized over the indolo[3,2-*b*]indole unit with a slight overlap on the π -spacer fragments, while the LUMO is predominantly localized on the acceptor cyanoacrylic acid. From the ground and excited state electron density distribution shown in Fig. 4, it is quite evident that there is sufficient charge separation between the donor and acceptor and the LUMO electron density is localized over the cyanoacrylic acid functionality, leading to better injection of the excited state charge carriers. The other orbitals involved in transitions are given in Fig. S10 in the ESI.† The HOMO–LUMO gaps were calculated to be between 2.45 and 2.53 eV. The HOMO of all the dyes was found to be between -5.09 and -5.22 eV. These results match what

Fig. 4 Schematic representation of electronic distributions observed in frontier orbitals (HOMO and LUMO) of IID dyes using DFT/B3LYP/6-311G(d,p) with band gap values.

Table 2 Comparison of the absorption properties of the dyes with the simulated excitation energy, oscillator strength, percentage contributions of the orbital density for different transitions and dipole moments

Dyes	Experimental		Theoretical (B3LYP-6311g**)		Composition	μ (Debye)
	λ_{max} (nm)	ε (M ⁻¹ cm ⁻¹)	λ (nm)	f		
IID-1	357	20 620	364 (3.40 eV)	0.56	HOMO $\rightarrow$ LUMO (99.16%) HOMO-1 $\rightarrow$ LUMO (99.66%) HOMO-2 $\rightarrow$ LUMO (89.60%)	8.0
IID-2	385	32 960	383 (3.24 eV)	0.43	HOMO $\rightarrow$ LUMO (98.37%) HOMO-1 $\rightarrow$ LUMO (96.38%) HOMO-2 $\rightarrow$ LUMO (93.73%)	7.4
IID-3	447	35 703	471 (2.63 eV)	0.36	HOMO $\rightarrow$ LUMO (98.24%) HOMO-1 $\rightarrow$ LUMO (95.12%) HOMO-2 $\rightarrow$ LUMO (93.56%)	6.5

we observed from the photophysical and electrochemical studies with the corresponding **IID** dyes.

To gain deeper insight into the electron density distribution in each dye, the partial electron density contribution from the respective frontier orbitals were calculated and the data is provided in Table 2. As can be seen from the table, the major low energy transition is contributed by the excitation of charge carriers from HOMO, HOMO-1, and HOMO-2 of the **IID** dyes to the LUMO, which is basically the charge transfer from the indolo[3,2-*b*]indole donor to the cyanoacrylic acid acceptor. The TDDFT results (Fig. S11, ESI[†]) are almost in good agreement with the experimental values as given in Table 2. The dipole moments are given in Table 2, which also indicate a large charge separation for the dye **IID-1**, employing benzene as the π -spacer and giving a dipole moment of 8.0 D. The thiophene-substituted dye **IID-2** displayed a dipole moment of 7.4 D and the smallest dipole moment was exhibited by **IID-3**, around 6.5 D. A better charge separation along with a slightly twisted structure that keeps the oxidized species in the electrolyte from getting proximal to the TiO₂ surface alleviates dye aggregation and renders better lifetime and photovoltaic performance for **IID-1** as compared to the other two dyes, which are discussed in detail in the following section.

3.4 Photovoltaic performance

To explore the potential of the newly synthesized indolo[3,2-*b*]indole dyes [**IID-1**, **IID-2** and **IID-3**] to be used as sensitizers in dye solar cells, devices were fabricated and the photovoltaic performances were evaluated using the standard (AM 1.5G, 100 mW cm⁻²) simulated solar spectrum employing an electrolyte composed of 0.5 M BMII, 0.1 M LiI, 0.03 M I₂ and 0.5 M tbp in acetonitrile. Detailed optimizations were carried out by fabricating devices with and without co-adsorbent (chenodeoxycholic acid, CDCA), and also by systematically varying the co-adsorbent concentrations (5 mM, 10 mM and 20 mM), so as to study the effect of aggregation on photovoltaic performance. The current-voltage curves and the tabulated results are summarized in Fig. S12 and Table S1, ESI[†]. All three dyes displayed their best performance in the presence of 20 mM CDCA. From the results, it is quite clear that the dyes are prone to aggregation and the best performance was obtained in the presence of co-adsorbent CDCA (20 mM). The current density *versus* voltage

Fig. 5 Current density–voltage characteristics of DSCs based on **IID-1**, **IID-2**, and **IID-3** under one sun illumination (AM 1.5G).

(*J*-*V*) results for the optimized solar cells fabricated using **IID-1**, **IID-2**, and **IID-3** as sensitizers are shown in Fig. 5 and the tabulated values are given in Table 3. The benzene substituted dye, **IID-1**, outperformed the other dyes (**IID-2** and **IID-3**) giving a power conversion efficiency of $2.38 \pm 0.11\%$ ($J_{\text{sc}} = 5.51 \pm 0.33$ mA cm⁻², $V_{\text{oc}} = 620 \pm 2$ mV, and FF = 69 ± 0.9), whereas **IID-2** showed a power conversion efficiency of $2.00 \pm 0.07\%$ ($J_{\text{sc}} = 5.22 \pm 0.21$ mA cm⁻², $V_{\text{oc}} = 570 \pm 8$ mV and FF = 67 ± 0.5) and **IID-3** displayed a power conversion efficiency of $1.71 \pm 0.12\%$ ($J_{\text{sc}} = 4.60 \pm 0.32$ mA cm⁻², $V_{\text{oc}} = 540 \pm 6$ mV and FF = 69 ± 0.5). Fig. S13 (ESI[†]) shows the IPCE spectra of **IID-1**, **IID-2**, and **IID-3**. Even though there is an extended absorption in the IPCE spectra for **IID-2** and **IID-3** from 400 to 600 nm with higher molar extinction coefficients, the device fabricated with **IID-1** showed better current, voltage and fill factor leading to improved photovoltaic performance.

To probe the loss in photocurrent and photovoltage for **IID-2** and **IID-3**, we explored the interfacial charge transfer dynamics

Table 3 Solar cell characteristics of DSCs based on **IID-1**, **IID-2**, and **IID-3**

Dyes	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	Efficiency (%)
IID-1	5.51 ± 0.33	620 ± 2	69 ± 0.9	2.38 ± 0.11
IID-2	5.22 ± 0.21	570 ± 8	67 ± 0.5	2.00 ± 0.07
IID-3	4.60 ± 0.32	540 ± 6	69 ± 0.5	1.71 ± 0.12

at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface using various small and large perturbation techniques so as to understand in more detail the factors contributing to lower performance on varying the π -spacers. Interestingly, there is a remarkable difference in voltage between **IID-1**, **IID-2**, and **IID-3**. To unravel the mechanism leading to this voltage difference, we carried out

open-circuit voltage decay (OCVD) and intensity modulated photovoltage spectroscopy (IMVS). Both OCVD and IMVS measurements were used to study the lifetime (τ_n) resulting from the recombination of electrons in the conduction band with the oxidized species present in the electrolyte. The average time that the electrons stay in the TiO_2 conduction band and sub band gap states before getting recombined with the oxidized species present in the electrolyte determines the lifetime. The higher the lifetime, the better will be the voltage. Lifetime is estimated from OCVD measurements using the equation

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1}$$

where k_B denotes the Boltzmann constant, T stands for temperature and e corresponds to the electron charge.^{58,59} OCVD measurements carried out on DSCs fabricated using **IID-1**, **IID-2**, and **IID-3** are shown in Fig. 6a. From the OCVD plot, it is quite clear that **IID-1** has a better lifetime followed by **IID-2** and **IID-3**, respectively, which corresponds to the same trend we observed with the open circuit voltage for these devices. Lifetime was calculated from the IMVS measurement using the

relation, $\tau_n = \frac{1}{2\pi f_m}$, where, f_m is the frequency maximum of the

Bode plot.^{60,65} Lifetime as a function of light intensity is shown in the Fig. 6b, measured using the IMVS technique. Both OCVD and IMVS measurements displayed the same lifetime trend. **IID-1** showed a better lifetime followed by **IID-2** and **IID-3**. Having thiophene (**IID-2**) and furan (**IID-3**) closer to TiO_2 enhances the recombination in these dyes as evident from OCVD and IMVS results in comparison to benzene (**IID-1**), which displayed better open circuit potential. To further investigate the variation in lifetime exhibited by changing the π -spacer for these indolo[3,2-*b*]-indole dyes, we performed electrochemical impedance spectroscopic measurements.

The electrochemical impedance spectroscopy of DSCs were measured in the dark from 100 kHz to 0.1 Hz. Nyquist plots of DSC had three semicircles, the first semicircle corresponds to the counter electrode (Pt)/electrolyte interface, the second semicircle corresponds to the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface and the third one corresponds to the diffusion of the oxidized

Fig. 6 (a) Lifetime plotted as a function of voltage for **IID** dyes obtained from OCVD measurement. (b) Lifetime as a function of LED current measured using the IMVS technique for the three **IID** dyes.

Fig. 7 (a) Nyquist plots of DSCs fabricated using **IID-1**, **IID-2**, and **IID-3** as sensitizers at -0.55 V under forward bias in the dark. (b) Equivalent circuit used for fitting the data.

and reduced species in the electrolyte, respectively. Fig. 7a shows the Nyquist plots of DSCs fabricated using **IID-1**, **IID-2**, and **IID-3** at 0.55 V under forward bias conditions. The third semicircle is not present due to the fast diffusion of the iodide electrolyte. The Nyquist plots were fitted using the Randles equivalent circuit as shown in Fig. 7b.²⁰ The charge transfer resistance (R_{ct}) was calculated from the equivalent circuit. The dye having benzene as π -spacer (**IID-1**) showed an R_{ct} value of 538 Ω , which is higher than **IID-2** (209 Ω) and **IID-3** (178 Ω) and is consistent with the V_{oc} values **IID-1** (620 mV) > **IID-2** (570 mV) > **IID-3** (540 mV). The better recombination resistance results in more hindrance to charge recombination, thereby pointing towards higher electron lifetime and higher photovoltage. Electron lifetime was calculated using the equation $\tau_n = R_{ct} \times C_{\mu}$. For the three indolo[3,2-*b*]indole devices, the calculated electron lifetime values showed an increasing trend in the order **IID-3** (3.29 ms) < **IID-2** (6.01 ms) < **IID-1** (6.88 ms). The observed variation in lifetime is in tune with the results obtained from OCVD and IMVS measurements, supporting the trend observed in device performance. The present work is in contrast to the latest report by Delcamp *et al.* on the effect of iodine binding with thiophene and furan π -spacers.⁶¹ They successfully displayed halogen bonding of S to I₂, employing thiophene as the spacer, which ultimately resulted in lower J_{sc} and V_{oc} values leading to lower photovoltaic performance relative to the furan spacer employing triphenylamine-based D35 analogous dyes. In the present study we show that in addition to the binding of iodine with the heteroatoms, other factors such as the nature of the donor, dihedral angle and aggregation can also contribute to determining the photovoltaic performance when we interchange the spacers.

4. Conclusions

Indolo[3,2-*b*]indole based D- π -A dyes employing benzene, thiophene, and furan as conjugated π -spacers were synthesized by employing a much simpler synthetic protocol in comparison to the literature reports. The role of π -spacers in controlling the interaction between the donor and acceptor, along with its role in establishing the optical, electrochemical and device properties were investigated in detail. The newly synthesized indolo[3,2-*b*]indole based dye with benzene as π -spacer delivered an efficiency of $2.38 \pm 0.11\%$, which serves as a promising start for a new fused heterocyclic unit to be introduced as a donor in DSC. It is quite interesting to realize the effects of conjugated π -spacers such as benzene, thiophene and furan in regulating the optoelectronic properties towards determining the photovoltaic performance. A more planar geometry leads to more aggregation, which triggers recombination and brings about lower performance, engaging thiophene and furan-substituted dyes (**IID-2** and **IID-3**). A slightly twisted conformation for the benzene substituted dye **IID-1** helped in effectively preventing oxidized from species coming closer to the semiconductor and adroitly alleviating dye aggregation by obstructing the formation of π -stacks, rendering **IID-1** a better lifetime and giving rise to superior solar cell

performance in terms of photocurrent, photovoltage and power conversion efficiency among the **IID** series. We are currently exploring the possibilities of tuning the spectral distribution in a way to further improve the performance of IID dyes.

Author contributions

PVS and JJ synthesized the molecules and compiled all the synthetic data. NPR and CMV supported in carrying out the synthesis of respective dyes. JV fabricated the devices and carried out characterization with support from SCP. SCP and SS analyzed the PV data and wrote the PV section. SL performed the photophysical and electrochemical measurements with supervision from SS. RKM carried out the DFT analysis. N. U. K. N co-ordinated the work. SS directed the entire research, compiled and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J. Gong, K. Sumathy, Q. Qiao and Z. Zhou, *Renewable Sustainable Energy Rev.*, 2017, **68**, 234–246.
- 2 M. Grätzel, *Inorg. Chem.*, 2005, **44**, 6841–6851.
- 3 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595–6663.
- 4 M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, J. Hua, S. M. Zakeeruddin, J. E. Moser, M. Grätzel and A. Hagfeldt, *Nat. Photonics*, 2017, **11**, 372–378.
- 5 Y. Cao, Y. Liu, S. M. Zakeeruddin, A. Hagfeldt and M. Grätzel, *Joule*, 2018, 1–10.
- 6 Z. Ning, Y. Fu and H. Tian, *Energy Environ. Sci.*, 2010, **3**, 1170–1181.
- 7 M. Liang and J. Chen, *Chem. Soc. Rev.*, 2013, **42**, 3453–3488.
- 8 M. Urbani, M. Grätzel, M. K. Nazeeruddin and T. Torres, *Chem. Rev.*, 2014, **114**, 12330–12396.
- 9 S. Soman, M. A. Rahim, S. Lingamoorthy, C. H. Suresh and S. Das, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23095–23103.
- 10 B. Pashaei, H. Shahroosvand, M. Graetzel and M. K. Nazeeruddin, *Chem. Rev.*, 2016, **116**, 9485–9564.

- 11 J. Wang, K. Liu, L. Ma and X. Zhan, *Chem. Rev.*, 2016, **116**, 14675–14725.
- 12 J. S. Ni, T. Y. Chiu, W. S. Kao, H. J. Chou, C. C. Su and J. T. Lin, *ACS Appl. Mater. Interfaces*, 2016, **8**, 23066–23073.
- 13 Y. K. Eom, S. H. Kang, I. T. Choi, Y. Yoo, J. Kim and H. K. Kim, *J. Mater. Chem. A*, 2017, **5**, 2297–2308.
- 14 M. V. Vinayak, T. M. Lakshmykanth, M. Yoosuf, S. Soman and K. R. Gopidas, *Sol. Energy*, 2016, **124**, 227–241.
- 15 K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa and M. Hanaya, *Chem. Commun.*, 2015, **51**, 15894–15897.
- 16 Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li and P. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 3799–3802.
- 17 Z. Yao, M. Zhang, R. Li, L. Yang, Y. Qiao and P. Wang, *Angew. Chem., Int. Ed.*, 2015, **54**, 5994–5998.
- 18 M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 2944.
- 19 Y. Cao, Y. Saygili, A. Ummadisingu, J. Teuscher, J. Luo, N. Pellet, F. Giordano, S. M. Zakeeruddin, J. E. Moser, M. Freitag, A. Hagfeldt and M. Grätzel, *Nat. Commun.*, 2017, **8**, 15390.
- 20 M. V. Vinayak, M. Yoosuf, S. C. Pradhan, T. M. Lakshmykanth, S. Soman and K. R. Gopidas, *Sustainable Energy Fuels*, 2018, **2**, 303–314.
- 21 D. X. Zhao, L. Y. Bian, Y. X. Luo, M. D. Zhang, H. Cao and M. D. Chen, *Dyes Pigm.*, 2017, **140**, 278–285.
- 22 X. Li, B. Xu, P. Liu, Y. Hu, L. Kloo, J. Hua, L. Sun and H. Tian, *J. Mater. Chem. A*, 2017, **5**, 3157–3166.
- 23 Y. Wang, Z. Zheng, T. Li, N. Robertson, H. Xiang, W. Wu, J. Hua, W. H. Zhu and H. Tian, *ACS Appl. Mater. Interfaces*, 2016, **8**, 31016–31024.
- 24 Z. Shen, J. Chen, X. Li, X. Li, Y. Zhou, Y. Yu, H. Ding, J. Li, L. Zhu and J. Hua, *ACS Sustainable Chem. Eng.*, 2016, **4**, 3518–3525.
- 25 P. Dai, L. Yang, M. Liang, H. Dong, P. Wang, C. Zhang, Z. Sun and S. Xue, *ACS Appl. Mater. Interfaces*, 2015, **7**, 22436–22447.
- 26 S. Qu, B. Wang, F. Guo, J. Li, W. Wu, C. Kong, Y. Long and J. Hua, *Dyes Pigm.*, 2012, **92**, 1384–1393.
- 27 J. H. Delcamp, Y. Shi, J. H. Yum, T. Sajoto, E. Dell'Orto, S. Barlow, M. K. Nazeeruddin, S. R. Marder and M. Grätzel, *Chem. – Eur. J.*, 2013, **19**, 1819–1827.
- 28 O. Gidron and M. Bendikov, *Angew. Chem., Int. Ed.*, 2014, **53**, 2546–2555.
- 29 M. Cariello, S. M. Abdalhadi, P. Yadav, J. D. Decoppet, S. M. Zakeeruddin, M. Grätzel, A. Hagfeldt and G. Cooke, *Dalton Trans.*, 2018, **47**, 6549–6556.
- 30 R. Yan, X. Qian, Y. Jiang, Y. He, Y. Hang and L. Hou, *Dyes Pigm.*, 2017, **141**, 93–102.
- 31 M. Paramasivam, R. K. Chitumalla, S. P. Singh, A. Islam, L. Han, V. Jayathirtha Rao and K. Bhanuprakash, *J. Phys. Chem. C*, 2015, **119**, 17053–17064.
- 32 S. Chaurasia, J.-S. Ni, W.-I. Hung and J. T. Lin, *ACS Appl. Mater. Interfaces*, 2015, **7**, 22046–22057.
- 33 S. A. Samsoniya and M. V. Trapaidze, *Russ. Chem. Rev.*, 2007, **76**, 313–326.
- 34 H. Zhao, L. Jiang, H. Dong, H. Li, W. Hu and B. S. Ong, *ChemPhysChem*, 2009, **10**, 2345–2348.
- 35 H. Jiang, H. Zhao, K. K. Zhang, X. Chen, C. Kloc and W. Hu, *Adv. Mater.*, 2011, **23**, 5075–5080.
- 36 Y. Jin, K. Kim, S. Song, J. Kim, J. Kim, H. P. Sung, K. Lee and H. Suh, *Bull. Korean Chem. Soc.*, 2006, **27**, 1043–1047.
- 37 L. Qiu, C. Yu, N. Zhao, W. Chen, Y. Guo, X. Wan, R. Yang and Y. Liu, *Chem. Commun.*, 2012, **48**, 12225–12227.
- 38 Y.-Y. Lai, J.-M. Yeh, C.-E. Tsai and Y.-J. Cheng, *Eur. J. Org. Chem.*, 2013, 5076–5084.
- 39 I. Cho, S. K. Park, B. Kang, J. W. Chung, J. H. Kim, K. Cho and S. Y. Park, *Adv. Funct. Mater.*, 2016, **26**, 2966–2973.
- 40 J. Sim, K. Do, K. Song, A. Sharma, S. Biswas, G. D. Sharma and J. Ko, *Org. Electron.*, 2016, **30**, 122–130.
- 41 M. M. Murray, D. A. Kaisaki, W. Chang, D. A. Dougherty and P. Kaszynski, *J. Am. Chem. Soc.*, 1994, **116**, 8152–8161.
- 42 P. Ruggli and H. Zeslin, *Helv. Chim. Acta*, 1935, **18**, 845–852.
- 43 A. N. Grinev and S. Y. Ryabova, *Chem. Heterocycl. Compd.*, 1982, **18**, 153–154.
- 44 P. Kaszynski and D. A. Dougherty, *J. Org. Chem.*, 1993, **58**, 5209–5220.
- 45 L. Qiu, X. Wang, N. Zhao, S. Xu, Z. An, X. Zhuang, Z. Lan, L. Wen and X. Wan, *J. Org. Chem.*, 2014, **79**, 11339–11348.
- 46 M. A. Truong and K. Nakano, *J. Org. Chem.*, 2015, **80**, 11566–11572.
- 47 H. E. Ho, K. Oniwa, Y. Yamamoto and T. Jin, *Org. Lett.*, 2016, **18**, 2487–2490.
- 48 L. H. Leijendekker, J. Weweler, T. M. Leuther and J. Streuff, *Angew. Chem., Int. Ed.*, 2017, **56**, 6103–6106.
- 49 P. V. Santhini, S. A. Babu, R. A. Krishnan, E. Suresh and J. John, *Org. Lett.*, 2017, **19**, 2458–2461.
- 50 P. V. Santhini, R. A. Krishnan, S. A. Babu, B. S. Simethy, G. Das, V. K. Praveen, S. Varughese and J. John, *J. Org. Chem.*, 2017, **82**, 10537–10548.
- 51 E. T. Pelkey, *Synthesis*, 1999, 1117–1122.
- 52 K. Lim, M. J. Ju, J. Na, H. Choi, M. Y. Song, B. Kim, K. Song, J. S. Yu, E. Kim and J. Ko, *Chem. – Eur. J.*, 2013, **19**, 9442–9446.
- 53 M. Akhtaruzzaman, Y. Seya, N. Asao, A. Islam, E. Kwon, A. El-Shafei, L. Han and Y. Yamamoto, *J. Mater. Chem.*, 2012, **22**, 10771–10778.
- 54 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 55 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
- 56 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. B. G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant,

- S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09, Revis. I.09*, Gaussian, Inc., Wallingford, CT, 2016.
- 57 R. Dennington, T. Keith and J. Millam, Semichem Inc., Shawnee Mission. KS, 2009.
- 58 S. Soman, Y. Xie and T. W. Hamann, *Polyhedron*, 2014, **82**, 139–147.
- 59 S. Sasidharan, S. Soman, S. C. Pradhan, K. N. N. Unni, A. A. P. Mohamed, B. N. Nair and H. U. N. Saraswathy, *New J. Chem.*, 2017, **41**, 1007–1016.
- 60 S. Soman, S. C. Pradhan, M. Yoosuf, M. V. Vinayak, S. Lingamoorthy and K. R. Gopidas, *J. Phys. Chem. C*, 2018, **122**, 14113–14127.
- 61 A. Baumann, H. Cheema, M. A. Sabuj, L. E. Mcnamara, Y. Zhang, A. Peddapuram, S. T. Nguyen, D. L. Watkins, N. I. Hammer, N. Rai and J. H. Delcamp, *Phys. Chem. Chem. Phys.*, 2018, **20**, 17859–17870.
- 62 N. Ruangsapapichat, M. Ruamyart, P. Kanchanarugee, C. Boonthum, N. Prachumrak, T. Sudyoadsuk and V. Promarak, *Dyes Pigm.*, 2018, **151**, 149–156.
- 63 L. Giribabu, R. K. Kanaparthi and V. Velkannan, *Chem. Rec.*, 2012, **12**, 306–328.
- 64 N. V. Krishna, J. V. S. Krishna, S. P. Singh, L. Giribabu, L. Han, I. Bedja, R. K. Gupta and A. Islam, *J. Phys. Chem. C*, 2017, **121**, 6464–6477.
- 65 S. C. Pradhan, A. Hagfeldt and S. Soman, *J. Mater. Chem. A*, 2018, **6**, 22204–22214.