# Benzimidazole-Indole-Chalcone Connected Methacrylate-Based Side Chain D- $\pi$ -A Polymer and its Application in Organic Photovoltaics

## Ramasamy Selvam, Kathavarayan Subramanian

Department of Chemistry, Anna University, Guindy, Chennai 600 025, India Correspondence to: K. Subramanian (E-mail: kathsubramanian@yahoo.com)

Received 9 September 2016; accepted 17 November 2016; published online in Wiley Online Library DOI: 10.1002/pola.28460

**ABSTRACT:** Herein, we report four metal-free organic polymethacrylates **(In-In-BzI)PMA**, **(Ac-In-BzI)PMA**, **(TPA-In-BzI)PMA**, and **(Py-In-BzI)PMA** with pendant chromophores donor- $\pi$ conjugated-acceptor (D- $\pi$ -A) molecular framework as photosensitizers for dye-sensitized solar cells (DSSCs). In which the donor-acceptor units are attached by an indole-chalcone extending side chain to inhibit back electron transfer and charge recombination; the  $\pi$ -linker component contains varied chalcone-based substituents to enhance the sunlightharvesting ability of the solar device. Photon-current cells based on the DSSC format were fabricated using the polymers

**INTRODUCTION** Polymers fabricated with push-pull effect have potential applications in many fields, including medical treatment, energy storage, electronic and optical applications because of their processability, high electrical conductivity, low cost, thermal and chemical stability.<sup>1</sup> In particular, optimizing the amount of charge transfer (CT) in a  $\pi$ -conjugated push-pull system has received immense attention for practical applications. There is currently a growing interest regarding the use of chalcone that is individually modified and/or associated with synthetic polymers as a building block in the fabrication of organic sensitizers suitable for photovoltaic applications due to their electron push-pull nature.<sup>2</sup> Conjugated polymers by their extended delocalized electron system have attracted broad academic and industrial interest for various optoelectronic devices. Specifically, their applications in polymer solar cells (PSCs), polymer light-emitting diodes (PLEDs), and organic field-effect transistors (OFETs) offer opportunities for a renewable energy supply as well as the development of display and information technologies.<sup>3</sup> To achieve high-performance organic sensitizers, many studies have focused on improving the following key properties: (i) improving the light harvesting ability and efficiency, (ii) molecular energy level, and (iii) decreasing the charge recombination reactions at the FTO/ TiO<sub>2</sub>/polymer/electrolyte interface.<sup>4</sup> In view of the polymer development, these have been mainly done by engineering their molecular structure and at either donor or acceptor moieties.

as sensitizers. The DSSC device assembled using **(TPA-In-BzI)PMA** exhibits a considerably better IPCE peak and J-V response, with an overall power conversion efficiency of 3.70% under the illumination of AM 1.5G (100 mW cm<sup>-2</sup>). © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

**KEYWORDS**: chalcone; charge transfer; donor–acceptor systems; DSSC; indole; pendant chromophore; poly(methacrylate); radical polymerization; thermal properties

More recently, multichromophore sunlight-harvesting assemblies based on a wide range of designs have been explored (i.e., polymers, dendrimers, peptides, porphyrin arrays).<sup>5</sup> Due to the intrinsic heterogeneity of the TiO<sub>2</sub>-mesoporous semiconductor surface and polymer architectures, the dynamics are inherently complex. Thus, a detailed understanding of the assembly and dynamical phenomena that ensue following sunlight absorption is paramount in the rational design of these polymer architectures. The design of highly efficient organic dyes involves a donor connected to an electron acceptor through an ethenyl or keto-vinyl bridge which allows fine-tuning of optical and electrochemical properties.<sup>6</sup> Four donor units viz., indole, acridine, triphenylamine and pyrene, and the acceptor unit benzimidazole are often chosen because of its strong electron-withdrawing ability' have been successfully reported. One particular approach was illustrated in which different donor units,  $\pi$ -bridges, and acceptor resulted in different electron recombination and thus affected the cell performances by introducing polycyclic aromatic hydrocarbons (PAHs) and ethenyl or keto-vinyl groups to the parent structure of polymers as  $\pi$ -bridges.<sup>8</sup> This could steer the HOMO and LUMO levels, as well as the band gap of the resulting polymers, which is a significant difference in the redox potential of the resulting polymers.<sup>9</sup> Recently, researchers have been showing much interest in the chemical synthesis and characterization of chalcone

Additional Supporting Information may be found in the online version of this article.

© 2017 Wiley Periodicals, Inc.



1

based conjugated polymers (CPs) due to their high thermal stability, good fluorescence quantum yield, and strong electron donor ability. Several examples of chalcone have been successfully used as highly efficient electroluminescent materials, building organic thin-film transistors, non-linear optics, photorefractive polymers, holographic recording materials, biological macromolecules and their copolymers for photovoltaic applications.<sup>10</sup> One approach involves the preparation of side-chain functionalized polymethacrylate with 5-nitro-benzimidazole as anchoring/acceptor unit to promote chemisorption of the polymer sensitizers on  $TiO_2$ through chalcone spacer, which resulted in photovoltaic performances reaching from  $0.84^{11}$  to 3.70%.

In the present study, four novel metal-free conjugated D- $\pi$ -A type methacrylate polymers (**P1-P4**) have been synthesized based on benzimidazole-indole-chalcone (BzI-In-Chalcone) system by the process of free radical polymerization using AIBN, consisting of the electron-donating indole, acridine, triphenylamine, and pyrene as the donor unit and strong electron-withdrawing benzimidazole as the terminal acceptor (Fig. 1). Introduction of indole and chalcone at the middle of the polymer was expected to have intramolecular charge transfer (ICT). The synthesized polymers were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Vis spectroscopy, and cyclic voltammetry to obtain thermal, optical, and electrochemical data. Finally the synthesized polymers were applied as a dye sensitizer towards fabrication of DSSCs.

#### **EXPERIMENTAL**

# **Instrumentation and Measurements**

<sup>1</sup>H- and the <sup>13</sup>C-NMR spectra were recorded on a Bruker 500 MHz spectrometer using tetramethylsilane as internal standard. FT-IR spectra were recorded by Perkin-Elmer FT-IR spectrometer RXI using KBr pellets. UV-Visible spectra were recorded on a UV-1601 Shimadzu UV-Visible spectrophotometer. Thermogravimetric analysis (TGA) of the polymer was carried out by a Mettler 851e TGA under nitrogen atmosphere at a heating rate of 10 °C/min. Transition temperatures  $(T_g)$  were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 calorimeter at a heating rate of 5 °C min<sup>-1</sup>. The molecular weights and the corresponding polydispersity index values of polymers were determined by gel permeation chromatography (GPC) with tetrahydrofuran as an eluent and mono disperse polystyrene standards used for calibration. Gas chromatography-mass spectrometry (GC-MS) was used to record GC-MS spectra by JEOL GCMATE II GC-MS. The cyclic voltammograms reported here were recorded using an AUTOLAB PGSTAT302N at room temperature in a conventional three-electrode system such as glassy carbon working electrode, Ag/AgCl reference electrode and platinum counter electrode at room temperature in nitrogen-purged acetonitrile (MeCN) at room temperature. Tetrabutylammonium perchlorate (TBAP) (0.1 M) was used as the supporting electrolyte and potential scanning from -0.8 to +1.5 V with a scan rate of 50 mV s<sup>-1</sup> was carried out. HOMO energy levels were estimated relative to



**FIGURE 1** Schematic representation of organic D- $\pi$ -A system featuring ICT. [Color figure can be viewed at wileyonlinelibrary.com]

the energy level of the ferrocene (Fc/Fc<sup>+</sup>) reference (4.8 eV below vacuum level). Electrochemical impedance spectroscopy (EIS) measurements were done under 100 mW/cm<sup>2</sup> light illumination by using an Autolab PGSTAT302N potentiostat/ galvanostat-84610. The impedance spectra were recorded with a frequency ranging between 0.1 Hz and 10 kHz at their open circuit potential (OCP).

#### Synthesis

The synthesis routes are shown in Schemes 1 and 2.

## Synthesis of 4-Bromo-2-(5-Nitro-1H-Benzoimidazol-2-Yl) Phenol

A mixture of 5-bromo-2-hydroxybenzaldehyde (2 g, 0.009 mol) and 4-nitrobenzene-1,2-diamine (1.8284 g, 0.012 mol) and ammonium acetate in the presence of acetic acid were refluxed for 24 h.<sup>12</sup> After that the reaction mixture was poured into cold water (100 mL) and the resulting precipitate was collected and purified by column chromatography (SiO<sub>2</sub>, 3:1, EtOAc/hexane) to obtain the desired product as yellow coloured solid with yield: (2.4 g, 65%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 4.32 (s, 1H), 4.92 (s, 1H), 7.12–8.05 (m, Ar-H).<sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 113.3, 118.2, 124.6, 145.8, 152.2, and 164.9. FT-IR (KBr pellet, cm<sup>-1</sup>): 3444, 3214, 3051, 2840, 2242, 1674, 1526, 1425, 1261, 1203, 1173, 1048, 1027, 960, 813. ANAL. CALCD. for C<sub>13</sub>H<sub>8</sub>BrN<sub>3</sub>O<sub>3</sub>: C, 46.73; H, 2.41; Br, 23.91; N, 12.58; O, 14.37. Found: C, 47.92; H, 3.70; Br, 25.44; N, 13.95; O, 15.82. GC-MS ANAL. CALCD. for C<sub>13</sub>H<sub>8</sub>BrN<sub>3</sub>O<sub>3</sub>: 334.12. Found: 335.51 [M + H]<sup>+</sup>.

## Synthesis of 1-(1-(4-Hydroxy-3-(5-Nitro-1H-Benzoimidazol-2-Yl)Phenyl)-1H-Indol-3-Yl)Ethanone

A mixture of 3-acetylindole (1 equiv.) compound 1 (1.2 equiv.), *trans*-1,2-diaminocyclohexane (0.1 equiv.), and  $K_3PO_4$  (5.0 equiv.)



SCHEME 1 Synthetic routes of compounds (3a-3d) reagents and conditions: (i) AcOH/reflux, (ii) K<sub>3</sub>PO<sub>4</sub>/Cul/1,2-diaminocycloheane/ DMF at 110 °C, (iii) 40% NaOH/MeOH.

and copper powder (1 equiv.) in dry DMF (25 mL) were heated at 110 °C with stirring for 48 h under nitrogen atmosphere.<sup>13</sup> Before the reaction was cooled, the hot reaction mixture was filtered through celite to remove the copper powder and inorganic salts. Removal of the solvent under reduced pressure gave the precursor as a crude material, which was purified by column chromatography (SiO<sub>2</sub>, 4:1, CHCl<sub>3</sub>/MeOH) to obtain the desired compound 2 as yellow coloured solid with yield: (2.4 g, 65%).

Polymer

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 2.12 (s, 3H), 4.48 (s, 1H), 4.93 (s, 1H), 7.10–8.55 (m, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 29.1, 113.4, 115.1, 116.8, 118.1, 119.1, 120.3, 121.1, 123.1, 126.8,128.3, 129.0, 135.2, 139.8, 144.1, 147.6, 150.1, 156.1, 186.2. FT-IR

(KBr pellet, cm<sup>-1</sup>): 3343, 3220, 3051, 2922, 2851, 2214, 1755, 1663, 1525, 1510, 1448, 1379, 1232, 1140, 1089, 963, 784. ANAL. CALCD. for C<sub>23</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 66.99; H, 3.91; N, 13.59; O, 15.52. Found: C, 67.19; H, 4.12; N, 14.96; O, 16.12. GC-MS Anal. Calcd. for  $C_{23}H_{16}N_4O_4$ : 412.40. Found: 413.51  $[M + H]^+$ .

#### Synthesis of Precursor (3a-3d)

#### General Procedure for the Synthesis of Precursor

A solution of 1 mole of compound 2 and 1 mole of sodium hydroxide in methanol was constantly stirred at room temperature. Then 1 mole of the corresponding aldehyde was dissolved in the required amount of methanol; it was slowly added with constantly stirred solution for 4 h.14 After that the reaction mixture was refluxed for 12 h. After cooling to





**SCHEME 2** Synthesis of polymers **(P1–P4)** reagents and conditions: (iv) methacryloyl chloride/DCM at 0 °C, (v) ACBN/THF at 70 to 75 °C. [Color figure can be viewed at wileyonlinelibrary.com]

room temperature, the mixture was poured into cold water and neutralized with 10% HCl. The precipitate was filtered and washed with distilled water. Volatiles were removed under vacuum and purified by column chromatography (SiO<sub>2</sub>).

## 1-(1-(4-Hydroxy-3-(6-Nitro-1H-Benzoimidazol-2-Yl)Phenyl)-1H-Indol-3-Yl)-3-(1H-Indol-3-Yl)Prop-2-En-1-One (3a)

The precursor 3a was prepared using indole-3-carbaldehyde following the general procedure for the synthesis of precursor given above from compound 2. Pale yellow solid; yield 86%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 4.56 (s, 1H), 4.91 (s, 1H), 6.57 (d, 1H), 8.19 (d, 1H), 7.19–8.10 (m, Ar-H), 9.89 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 112.7, 115.2, 117.5, 119.2, 120.6, 121.1, 123.1, 125.8, 129.6, 131.0, 133.5, 135.8, 137.1, 141.4, 143.8, 145.6, 152.5, 157.8, 161.3, 185.7. FT-IR (KBr pellet, cm<sup>-1</sup>): 3390, 3230, 3051, 2962, 2290, 1740, 1633, 1585, 1450, 1279, 1149, 1032, 966, 814. ANAL. CALCD. for C<sub>32</sub>H<sub>21</sub>N<sub>5</sub>O<sub>4</sub>: C, 71.24; H, 3.92; N, 12.98; O, 11.86. Found: C, 72.99; H, 4.22; N, 13.86; O, 12.68. GC-MS ANAL. CALCD. for C<sub>32</sub>H<sub>21</sub>N<sub>5</sub>O<sub>4</sub>: 539.54. Found: 540.86 [M + H]<sup>+</sup>.

## 3-(Acridin-9-Yl)-1-(1-(4-Hydroxy-3-(6-Nitro-1H-Benzoimidazol-2-Yl)Phenyl)-1H-Indol-3-Yl)Prop-2-En-1-One (3b)

The precursor 3b was obtained using acridine-9-carbaldehyde following the general procedure for the synthesis of precursor given above from compound 2. Yellow solid; yield 80%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 4.45 (s, 1H), 5.10 (s, 1H), 6.90 (d, 1H), 7.19–8.0 (m, Ar-H), 8.16 (d, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 113.2, 119.2, 120.8, 123.1, 129.2, 131.8, 135.1, 142.4, 167.2, 182.7. FT-IR (KBr pellet, cm<sup>-1</sup>): 3412, 3340, 3093, 2967, 2840, 2216, 1769, 1636, 1523, 1455, 1364, 1198, 960, 824. ANAL. CALCD. for C<sub>37</sub>H<sub>23</sub>N<sub>5</sub>O<sub>4</sub>: C, 73.87; H, 3.85; N, 11.84;

0, 10.64. Found: C, 74.19; H, 4.12; N, 12.96; O, 11.59. GC-MS Anal. Calcd. for  $C_{37}H_{23}N_5O_4{:}$  601.61. Found: 602.86  $\left[M+H\right]^+{}.$ 

## 3-(4-(Diphenylamino)Phenyl)-1-(1-(4-Hydroxy-3-(6-Nitro-1H-Benzoimidazol- 2yl) Phenyl)-1H-Indol-3-Yl) Prop-2-En-1-One (3c)

The precursor 3c was synthesized using 4-(diphenylamino)benzaldehyde following the general procedure for the synthesis of precursor given above from compound 2. Yellow solid; yield 79%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ* ppm): 4.22 (s, 1H), 5.20 (s, 1H), 6.70 (d, 1H) 7.09–8.02 (m, ArH), 7.98 (d, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, *δ* ppm): 110.2, 112.5, 113.4, 115.7, 117.5, 119.3, 121.2, 123.5, 125.1, 127.8, 129.3, 130.5, 132.8, 137.1, 139.6, 145.4, 147.7, 149.5, 152.3, 156.6, 159.8, 164.1, 183.7. FT-IR (KBr pellet, cm<sup>-1</sup>): 3412, 3341, 3093, 3052, 2942, 2851, 2240, 1768, 1633, 1585, 1457, 1339, 1228, 1096, 940, 814. ANAL. CALCD. for C<sub>42</sub>H<sub>29</sub>N<sub>5</sub>O<sub>4</sub>: C, 75.55; H, 4.38; N, 10.49; O, 9.58. Found: C, 76.19; H, 5.52; N, 10.99; O, 10.12. GC-MS ANAL. CALCD. for C<sub>42</sub>H<sub>29</sub>N<sub>5</sub>O<sub>4</sub>: 667.71. Found: 667.87 [M + H]<sup>+</sup>.

## 1-(1-(4-Hydroxy-3-(6-Nitro-1H-Benzoimidazol-2-Yl)Phenyl)-1H-Indol-3-Yl)-3-(Pyren- 1-Yl)Prop-2-En-1-One (3d)

The precursor 3d was prepared using 1-pyrenealdehyde following the general procedure for the synthesis of precursor given above from compound 2. Pale yellow solid; yield 81%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 4.65 (s, 1H), 5.42 (s, 1H), 6.86 (s, 1H), 7.09-7.96 (m, ArH), 8.09 (d, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 108.1, 110.0, 112.2, 113.6, 115.2, 116.8, 119.2, 120.3, 121.5, 123.1, 125.8, 127.7, 129.0, 131.7, 133.4, 137.4, 140.2, 144.5, 147.8, 149.1, 155.1, 159.6, 167.2, 181.2. FT-IR (KBr pellet, cm<sup>-1</sup>): 3423, 3343, 3051, 2922, 2851, 2214, 1750, 1663, 1525, 1510, 1448, 1379, 1232, 1089, 969, 784. Anal. CALCD. for C<sub>40</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>: C, 76.91; H, 3.87; N, 8.97; O, 10.25. Found: C, 77.19; H, 4.52; N, 9.16; O, 11.12. GC-MS Anal. CALCD. for C<sub>40</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>: 624.64. Found: 625.88 [M + H]<sup>+</sup>.

JOURNAL OF POLYMER SCIENCE Chemistry

### Synthesis of Monomers (M1-M4)

## 4-(3-(3-(1H-Indol-3-YI)Acryloyl)-1H-Indol-1-YI)-2-(6-Nitro-1H-Benzoimidazol-2-YI)Phenyl Methacrylate (M1)

A double-necked flask was charged with a mixture of a compound 3a (2 g, 0.003 mol) dissolved in dry DCM and treated with freshly distilled acryloyl chloride (0.3 mL, 0.003 mol) in the presence of triethylamine, at 0 to 5 °C. The above mixture was stirred at room temperature in the presence of nitrogen atmosphere for 2 h.<sup>15</sup> The quaternary ammonium salt was filtered and the reaction mixture separated using excess of DCM. The monomer was purified by column chromatography (SiO<sub>2</sub>, EtOAc:hexane = 1:1) to afford the desired product as yellow coloured solid; yield 1.5 g (65%).

ANAL. CALCD. for  $C_{36}H_{25}N_5O_5$ : C, 71.16; H, 4.15; N, 11.53; O, 13.17. Found: C, 72.58; H, 5.34; N, 12.78; O, 14.49. GC-MS ANAL. CALCD. for  $C_{36}H_{25}N_5O_5$ : 607.61. Found: 608.89. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.62 (s, 3H), 4.90 (s, 1H), 5.95 (d, 1H), 6.17 (dd, 1H), 6.95 (d, 1H), 7.08–8.32 (m, ArH), 8.12 (d, 1H), 9.8 (s, 1H) (Supporting Information Fig. S5). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 36.8, 108.7, 110.1, 111.7, 112.7, 113.0, 115.3, 117.8, 119.5, 120.1, 121.4, 123.7, 125.6, 127.8, 129.0, 131.6, 133.8, 135.2, 138.6, 139.2, 143.5, 144.7, 149.6, 152.2, 158.8, 169.3, 181.9 (Supporting Information Fig. S6). FT-IR (KBr pellet, cm<sup>-1</sup>): 3390, 3250, 3051, 2963, 2280, 1710, 1637, 1450, 1257, 1175, 950, 813 (Supporting Information Fig. S1).

## 4-(3-(3-(Acridin-9-YI) Acryloyl)-1H-Indol-1-YI)-2-(6-Nitro-1H-Benzoimidazol-2-YI) Phenyl Methacrylate (M2)

The synthesis procedure of the monomer M2 was similar to that of M1 by using the compound 5b (2g, 0.004). After purification, a brown solid was obtained (1.8 mg, yield = 73%).

ANAL. CALCD. for  $C_{41}H_{27}N_5O_5$ : C, 73.53; H, 4.06; N, 10.46; O, 11.95. Found: C, 74.17; H, 5.10; N, 12.71; O, 13.17; S, 7.54. GC-MS ANAL. CALCD. for  $C_{41}H_{27}N_5O_5$ : 669.68. Found: 670.89. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.82 (s, 3H), 4.79 (s, 1H), 6.22 (d, 1H), 6.69 (dd, 1H), 7.19 (d, 1H), 7.24–8.05 (m, ArH), 8.22 (d, 1H) (Supporting Information Fig. S7). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 33.8, 109.4, 110.2, 114.7, 117.8, 119.0, 120.4, 121.8, 123.5, 125.2, 126.8, 128.1, 131.6, 135.1, 138.6, 139.8, 143.5, 147.8, 155.2, 168.3, 188.5 (Supporting Information Fig. S8). FT-IR (KBr pellet, cm<sup>-1</sup>): 3415, 3310, 3055, 2967, 2480, 2260, 1756, 1661, 1593, 1450, 1362, 1239, 1102, 966, 809 (Supporting Information Fig. S2).

## 4-(3-(3-(4-(Diphenylamino) Phenyl)Acryloyl)-1H-Indol-1-Yl)-2-(6-Nitro-1H-Benzoimidazol-2-Yl)Phenyl Methacrylate (M3)

Monomer M3 was synthesized by following the same procedure as that of M1 by using the compound 5c (2 g, 0.004). After purification, a yellow solid was obtained (1.7 mg, yield = 70%).

ANAL. CALCD. for  $C_{46}H_{33}N_5O_5$ : C, 75.09; H, 4.52; N, 9.52; O, 10.87. Found: C, 76.37; H, 5.19; N, 10.15; O, 11.97. GC-MS ANAL. CALCD. for  $C_{46}H_{33}N_5O_5$ : 735.78. Found: 736.91. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.72 (s, 3H), 4.99 (s, 1H), 6.08 (d, 1H), 6.55 (dd, 1H), 6.91 (d, 1H), 7.11–8.65 (m, Ar-H), 8.19 (d, 1H) (Supporting Information Fig. S9). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm):

33.4, 87.2, 110.2, 111.7, 112.5, 115.7, 117.7, 119.0, 121.5, 122.8, 124.1, 129.6, 131.0, 135.6, 139.4, 143.5, 148.4, 152.3, 158.2, 165.2, 171.4, 181.1 (Supporting Information Fig. S10). FT-IR (KBr pellet, cm<sup>-1</sup>): 3315, 3256, 3046, 2930, 2490, 2265, 1724, 1664, 1540, 1450, 1332, 1226, 1170, 1096, 965, 735 (Supporting Information Fig. S3).

## 2-(6-Nitro-1H-Benzoimidazol-2-Yl)-4-(3-(3-(Pyren-1-Yl) Acryloyl)-1H-Indol-1-Yl)Phenyl Methacrylate (M4)

A similar synthetic method was used to prepare monomer M4 from compound 5d (2 g, 0.004). After purification, a yellow solid was obtained (1.6 mg, yield = 68%).

ANAL. CALCD. for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>O<sub>5</sub>: C, 76.29; H, 4.07; N, 8.09; O, 11.55. Found: C, 77.17; H, 5.10; N, 9.71; O, 12.97. GC-MS ANAL. CALCD. for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>O<sub>5</sub>: 692.72. Found: 693.85. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 1.62 (s, 3H), 4.78 (s, 1H), 5.89 (d, 1H), 6.12 (dd, 1H), 6.87 (d, 1H), 8.12 (d, 1H), 7.20–8.10 (m, ArH) (Supporting Information Fig. S11). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 30.1, 110.3, 112.0, 113.6, 115.5, 117.7, 119.1, 120.2, 121.7, 122.8, 123.8, 125.1, 128.6, 129.7, 133.6, 135.6, 137.8, 139.5, 141.2, 145.6, 148.4, 151.2, 155.1, 158.3, 164.3, 172.9, 188.9 (Supporting Information Fig. S12). FT-IR (KBr pellet, cm<sup>-1</sup>): 3340, 3229, 3061, 2924, 2886, 2240, 1749, 1668, 1540, 1462, 1339, 1245, 1139, 1050, 968, 820 (Supporting Information Fig. S4).

#### Synthesis of Polymers (P1-P4)

## 4-(3-(3-(1H-Indol-3-YI)Acryloyl)-1H-Indol-1-YI)-2-(6-Nitro-1H-Benzoimidazol-2-YI)Phenyl Polymethacrylate (in-in-BzI)PMA (P1)

The methacrylate polymers were synthesized by free radical polymerization method, according to the literature.<sup>16</sup> Monomer (M1) and AIBN (0.5% wt of monomer) in 10 mL THF were taken in a polymerization tube and flushed with nitrogen for 10 min to remove the dissolved oxygen and, then the tube was sealed to ensure the inert atmosphere and kept in a thermostat at  $70 \pm 2$  °C. It was then filtered and after cooling to room temperature, the filtrate was poured into methanol. The precipitate was filtered and washed with methanol. The crude product was purified by dissolving in THF and precipitating into methanol to afford a yellow solid. (Yield 0.19 g, 45%).

FT-IR (KBr pellet, cm<sup>-1</sup>): 3358, 3290, 3055, 2950, 2820, 2229, 1757, 1682, 1593, 1510, 1448, 1319, 1226, 1176, 1018, 981, 820 (Supporting Information Fig. S1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.12 (d, 1H), 1.62 (m, 2H), 2.12 (m, 1H), 5.21 (s, 1H), 6.15 (1H, d), 7.12 (d, 1H), 8.10 (1H, d), 7.35-8.49 (m, Ar-H), 10.12 (s, 1H) (Supporting Information Fig. S13). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 29.6, 37.7, 41.5, 62.1, 109.4, 110.1, 112.6, 113.8, 115.4, 117.7, 118.9, 121.5, 123.8, 125.3, 127.2, 129.5, 131.2, 133.6, 134.7, 137.7, 139.2, 142.4, 145.2, 149.1, 151.5, 155.3, 158.2, 167.9, 172.6, 188.3 (Supporting Information Fig. S14).

## 4-(3-(3-(Acridin-9-YI)Acryloyl)-1H-Indol-1-YI)-2-(6-Nitro-1H-Benzoimidazol-2-YI)Phenyl Polymethacrylate (Ac-in-BzI)PMA (P2)

The polymer P2 was prepared from M2 by adapting the procedure similar to P1. It afforded a yellow solid (yield 52%).



FT-IR (KBr pellet, cm<sup>-1</sup>): 3340, 3310, 3045, 2921, 2840, 1748, 1673, 1593, 1518, 1430, 1367, 1223, 1161, 1013, 985, 810 (Supporting Information Fig. S2). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.09 (d, 3H), 1.35 (m, 2H), 2.13 (m, 1H), 4.96 (s, 1H), 6.67 (d, 1H), 8.21 (d, 1H), 7.21–8.65 (m, Ar-H) (Supporting Information Fig. S15). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 33.6, 38.8, 47.7, 63.2, 98.2, 110.2, 112.4, 114.4, 116.4, 117.7, 119.2, 121.8, 123.4, 125.6, 128.6, 131.2, 133.6, 135.7, 139.7, 141.2, 146.4, 149.0, 152.5, 156.6, 159.9, 164.5, 172.3, 189.3 (Supporting Information Fig. S16).

## 4-(3-(3-(4-(Diphenylamino) Phenyl)Acryloyl)-1H-Indol-1-Yl)-2-(6-Nitro-1H-Benzo Imidazol-2-Yl)Phenyl Polymethacrylate (TPA-in-Bzl)PMA (P3)

Polymer P3 was prepared from M3 by using the similar procedure as that of P1. A light brown solid was obtained (yield 52%).

FTIR (KBr pellet, cm<sup>-1</sup>): 3340, 3284, 3030, 2928, 2877, 2433, 2226, 1742, 1667, 1593, 1512, 1496, 1344, 1161, 1006, 958, 824 (Supporting Information Fig. S3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 1.28 (d, 3H), 1.62 (m, 2H), 2.37 (m, 1H), 4.86 (S, 1H), 6.75 (d, 1H), 8.22 (d, 1H), 7.35–8.69 (m, Ar-H) (Supporting Information Fig. S17). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 30.2, 34.2, 53.7, 97.1, 110.3, 112.8, 113.7, 115.5, 117.5, 119.4, 120.3, 123.6, 125.6, 127.4, 129.6, 131.2, 133.5, 135.3, 137.2, 139.7, 143.2, 145.4, 149.2, 152.1, 158.5, 162.9, 166.7, 174.4, 183.3 (Supporting Information Fig. S18).

## 2-(6-Nitro-1H-Benzoimidazol-2-Yl)-4-(3-(3-(Pyren-1-Yl)Acryloyl)-1H-Indol-1-Yl) Phenyl Polymethacrylate (Py-in-Bzl)PMA (P4)

Polymer P4 was prepared from M4 by using the similar procedure as that of P1. A light brown solid was obtained (yield 52%).

FTIR (KBr pellet, cm<sup>-1</sup>): 3390, 3264, 3098, 2928, 2877, 2226, 1762, 1667, 1593, 1512, 1455, 1321, 1161, 1006, 938, 824 (Supporting Information Fig. S4). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.27 (d, 3H), 1.65 (m, 2H), 2.19 (m, 1H), 4.25 (s, 1H), 6.31 (d, 1H), 7.20 (d, 1H), 7.32–8.49 (m, Ar-H) (Supporting Information Fig. S19). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 34.6, 41.7, 48.5, 92.2, 112.7, 114.2, 116.3, 119.6, 121.0, 123.3, 125.5, 127.6, 129.6, 131.2, 133.2, 134.7, 136.2, 139.2, 143.4, 145.1, 149.1, 151.5, 156.9, 159.4, 164.9, 175.3, 189.3 (Supporting Information Fig. S20).

#### **Device Fabrication and Photovoltaic Measurements**

The titanium oxide (TiO<sub>2</sub>) paste was coated onto the cleaned conducting glass substrate (fluorine-doped SnO<sub>2</sub> (FTO; sheet resistance10  $\Omega$  sq<sup>-1</sup>) according to the described procedure.<sup>17</sup> The DSSCs were fabricated in the following configuration: FTO/TiO<sub>2</sub>/polymer/Li1/Al. After making the films they were annealed at 400 °C for 1 h. For sensitization, the films were dipped in samples viz. solutions of modified or unmodified polymer in DMF for 24 h at room temperature. The films were then rinsed with DMF to remove excess polymeric dye on the surface and air-dried at room temperature. This was followed by redox electrolyte addition and top contact of aluminium

coated FTO. The electrolyte was composed of 0.5 M LiI, 0.05 M iodine (I2), and 0.5 M tetra-butylammonium hexafluorophosphate (TBAHFP) in 3-methoxypropionitrile which was injected in between the two electrodes.<sup>18</sup> Finally aluminium electrode was thermally evaporated through a second mask. The photoelectrochemical characterizations were measured by using modified light source 300 W Xe lamp (Oriel, 6258) equipped with an air mass (AM) 1.5 filter (Oriel, 81080 kit) and the light intensity was 100 mW/cm<sup>2</sup>. Fabricated solar cells were characterized by measuring current density-voltage (J-V) curves using a computer controlled Potentiostat/Galvanostat-84610. The monochromatic incident photon-to-current conversion efficiency (IPCE) spectra were measured for the solar cells with an Oriel 300 W Xe Arc lamp in combination with an Oriel Cornerstone 2601/4 monochromator as a function of wavelength.

## **RESULTS AND DISCUSSION**

## **Thermal Analysis**

Thermal properties of the polymers (P1-P4) were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA curves of polymer (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were carried out under  $N_2$  atmosphere and depicted in Figure 2(a). Their corresponding data were listed in Table 1. The glass transition temperature ( $T_{\rm g}$  °C) of polymers (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were determined by DSC, which obtained in the range of 119 to 135 °C [Fig. 2(b), Table 1]. The initial decomposition temperature (IDT) of polymers (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were 235, 210, 222, and 231 °C, respectively. The decomposition temperature  $(T_d)$  values of 309, 295, 302, and 312 °C were observed for benzimidazole-indolechalcone polymethacrylate ((Bz-In-chalcone)-PMA) respectively at 10% weight loss. All polymers have shown reasonably good thermal stability as display in Table 1. The degradation of polymers occurred in two stages. The first stage decomposition (210-350 °C) occurred due to the cleavage of the pendant chalcone group, and the second stage (450-720 °C) decomposition occurred due to the cleavage of the main chain bonds. TGA thermogram revealed that two distinct behaviors depend on the chalcone and polycyclic aromatic ring substituents. So the incorporation of different chalcone units bonded to benzimidazole-indole in the polymer backbone change the rigidity and planarity of the molecule and these affect the thermal property of the polymers.<sup>19</sup> These results showed that all the polymers (P1-P4) possess high thermal stability which could exploited for photovoltaic cells (PVC) and other optoelectronic devices.

#### Molecular Weight of Polymers (P1-P4)

Molecular weights of polymers (**P1-P4**) were determined by GPC in THF using polystyrene as a standard. The weight average ( $M_w$ ) molecular weight values of all the polymers, viz. (**In-In-BzI**)**PMA**, (**Ac-In-BzI**)**PMA**, (**TPA-In-BzI**)**PMA**, and (**Py-In-BzI**)**PMA** were ranging from 24,000 to 30,000. The number ( $M_n$ ) average molecular weight values of all the



**FIGURE 2** (a) TGA curves of polymers **P1-P4** under  $N_2$  condition. (b) DSC curves of polymers. [Color figure can be viewed at wileyonlinelibrary.com]

polymers (**P1-P4**) were in the range of 16,400 to 18,900, and polydispersity index (PDI) of polymers (**In-In-BzI**)**PMA**, (**Ac-In-BzI**)**PMA**, (**TPA-In-BzI**)**PMA**, and (**Py-In-BzI**)**PMA** obtained in the range 1.55 to 1.72 (Supporting Information Fig. S21). The theoretical polydispersity index value of the polymer produced via radical recombination and disproportionation reaction are 1.5 and 2.0 respectively,<sup>20</sup> and corresponding data were summarized in Table 1. The polydispersity index (PDI) value of the polymers (**P1-P4**) suggest that the chain termination tendency of the radical combination was strong than that of disproportionation reaction.

#### **Optical Properties**

The photophysical features of chalcone based polymers (P1–P4) were investigated by ultraviolet-visible (UV-Vis) absorption measurements in diluted DMF solution  $(10^{-5} \text{ M})$ . Figure 3 shows the absorption spectra of (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA polymers, and the results were summarized in Table 2. The more intense absorption band located in the range of 300 to 420 nm corresponds to the  $\pi$ - $\pi$ \* transition of the conjugated aromatic rings. The other weaker low-energy bands appeared as a shoulder between 430 and

540 nm which was attributed to the intramolecular charge transfer (ICT).<sup>21</sup> The lowest energy transition in chalcone possesses n- $\pi^*$  or a  $\pi$ - $\pi^*$  character<sup>22</sup> with a contribution from intramolecular charge transfer (ICT) which gives rise to a shoulder band in the absorption spectrum. The ICT absorption maxima  $(\lambda_{\text{max}})$  of (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA polymers showed (+40 nm red shift) push-pull effect between terminal donor substituent (chalconepolycyclic aromatic ring) and an acceptor benzimidazole unit of polymers due to the presence of extended conjugative delocalization within the chalcone-acceptor segment. Among the polymers (P1-P4), polymer (Ac-In-BzI)PMA and (TPA-In-BzI)PMA has the longest absorption band attributed to the presence of acridine and triphenylamine moiety; which facilitates the push-pull character of ICT.<sup>23</sup> The absorption bands of remaining polymers were significantly blue shifted. In addition, the absorption relating to benzimidazole-indole-chalcone polymers also stands evidence for donor-acceptor type polymers. There was a progressive redshift in the absorption profile reflecting the electron-withdrawing nature of benzimidazole unit. The molar extinction coefficients of the  $\pi$ - $\pi$ \* bands for (BzI-In-Chalcone) polymers were also investigated in DMF and the results are in the order of (Py-In-BzI) PMA < (In-In-BzI)PMA < (Ac-In-BzI)PMA < (TPA-In-BzI)PMA, which indicates that (Ac-In-BzI)PMA and (TPA-In-BzI)PMA possess the best light-harvesting ability. These indicate the existence of strong intramolecular interaction and ordering in these thin polymer films. On the contrary, a small red shift from the solution to solid was observed for (Ac-In-BzI)PMA and (TPA-In-BzI)PMA, which suggests that the aggregation could exist in solution for the polymer containing acridine and triphenylamine units. The optical band gaps estimated from the low-energy absorption onset wavelengths ( $E_g^{opt} = 1240/\lambda_{onset}$ ) of the polymer films were 3.06 eV for (In-In-BzI)PMA, 2.90 eV for (Ac-In-BzI)PMA, 2.76 eV for (TPA-In-BzI)PMA, and 2.98 eV for (Py-In-BzI)PMA.

Figure 3(b) displays the absorption spectra of the polymers on a  $TiO_2$  film; the absorption bands of **P1-P4** are red-shifted slightly compared with those measured in the solution, which can be attributed to the formation of a J-aggregation or polymer- $TiO_2$  interaction.<sup>24</sup> In addition, observed broadened absorption peaks which may be significantly due to the greater interaction between anchoring/acceptor group of polymers and nanocrystalline- $TiO_2$  surface.<sup>25</sup> Such broadening of the absorption in the

**TABLE 1** Molecular Weight and Thermal Properties of Polymers

Polymer	M <sub>w</sub> (g/mol) <sup>a</sup>	<i>M</i> <sub>n</sub> (g/mol) <sup>a</sup>	PDI	$T_{g}$ (°C) <sup>b</sup>	T <sub>d</sub> (°C) <sup>c</sup>
P1	29,700	18,900	1.57	132	309
P2	30,100	17,500	1.72	127	295
P3	27,800	16,400	1.69	119	302
P4	25,500	16,400	1.55	135	312

<sup>a</sup> Determined by gel permeation chromatography using polystyrene as a standard.

 $^{\rm b}$  Determined by DSC with a heating rate of 10 °C/min under nitrogen.

<sup>c</sup> The temperature at 10% weight loss under nitrogen.



ARTICLE



**FIGURE 3** UV-Vis absorption spectra of polymers (**P1–P4**), (a) in DMF solution, (b) on  $TiO_2$  nanoparticles. [Color figure can be viewed at wileyonlinelibrary.com]

visible region is suitable for fabrication of sunlight harvesting device (DSSC) with these polymeric dyes which leads to a better photocurrent. From the optical studies, it is clear that the **P4** polymer containing tri-phenylamine as a donor and benzimidazole with nitro segment as a  $\pi$ -linker as well as an anchoring/ acceptor group may be a good polymer-sensitizer upon compared to the other polymers (**P1, P2**, and **P4**) for DSSC application.

#### **Electrochemical Properties**

To understand the electronic structures of the BzI-In-Chalcone polymers (P1-P4) cyclic voltammetry (CV) was performed. Figure 4 shows the results of electrochemical measurements of the polymers in the potential range from -0.8 to 1.5 V. CV measurements showed that the potential of the positive irreversible process of oxidation, and both the shape of the curves and the individual oxidation potential peaks depend on the type of substituent in polymers. The electrochemical properties of the polymers were determined from the band gaps estimated from the absorption onset wavelength and the HOMO energy levels which were estimated from the cyclic voltammetry (CV). These values were useful to find out the thermodynamic feasibility of electron injection into the conduction band of the metal oxide from the HOMO level and polymer regeneration by the electrolyte.<sup>26</sup> The polymer solution was drop cast on a glassy carbon electrode and was used as the working electrode. The HOMO energy levels were determined by measuring

the onset oxidation potential ( $E_{ox}^{onset}$ ) of the polymer films. To obtain the oxidation potentials, the reference electrode was calibrated using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), which had a redox potential with an absolute energy level of -4.80 eV in vacuum; the potential of this external standard under the same conditions was 0.40 V versus Ag/Ag<sup>+</sup>. Figure 4 showed the cyclic voltammograms of the polymer films on the glassy carbon in 0.1 mol/L TBAP in MeCN medium.<sup>27</sup> The onset oxidation potential (E<sub>ox</sub><sup>onset</sup>) of (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were 0.79, 0.81, 0.78, and 0.79 V vs. Ag/Ag<sup>+</sup>, respectively. From  $E_{ox}^{onset}$  of the polymers, HOMO energy levels, as well as LUMO energy levels of the polymers, were calculated according to the equations:  $E_{\text{HOMO}} = -[E_{\text{ox}}^{\text{onset}} + 4.8] \text{ eV; } E_{\text{LUMO}} = [E_{\text{g}} + E_{\text{HOMO}}] \text{ eV; where } E_{\text{g}}$ stands for optical band-gap of the polymers (P1-P4) obtained from the absorption onset wavelengths of the polymers in UV-Vis absorption measurements. The results of the electrochemical measurements were tabulated in Table 2. The HOMO energy levels of polymers (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were -5.59, -5.68, -5.58, and -5.59 eV, respectively. The HOMO-LUMO energy diagrams of the polymers are shown in Figure 5. The LUMO energy levels of (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were -2.53, -2.78, -2.82, and -2.61 eV, respectively. The incorporation of indole-chalcone segment in the polymer structure is beneficial to bring down the LUMO energy level closer to TiO<sub>2</sub> conduction band and brought up

TABLE 2 Optical, Electrochemical Data, and HOMO, LUMO Energy Levels of Synthesized Polymers

Polymer	$\lambda_{abs} (nm)^a$	$\lambda_{abc} (nm)^{b}$	$E_{\rm ox}$ (vs. Fc) (V) <sup>c</sup>	$E_{\rm g}~({\rm eV})^{\rm d}$	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)
P1	348	381	0.66	3.06	-5.46	-2.40
P2	362	395	0.75	2.90	-5.61	-2.71
P3	351	417	0.79	2.76	-5.59	-2.83
P4	340	376	0.81	2.98	-5.68	-2.70

<sup>a</sup> Absorption of DMF solution.

<sup>b</sup> Absorption of films.

<sup>c</sup> Values determined by cyclic voltammetry.

<sup>d</sup> E<sub>gonset</sub>: optical band gap was calculated from UV-Vis spectra.



**FIGURE 4** The CV curves of polymers (**P1–P4**) in the ordered, the polymer films on Platinum electrode in 0.1 mol/L TBAP in MeCN medium scan rate 50 mV/s, Ag/AgCl–reference electrode. [Color figure can be viewed at wileyonlinelibrary.com]

the HOMO energy level closer to the electrolyte potential which narrows the band gap. The LUMO values of all polymer were occupied in the range of -2.53 to -2.82 eV, which is above than the conduction band edge of TiO<sub>2</sub> (-4.0 eV vs. vacuum).<sup>28</sup> The HOMO values of polymers were in between -5.58 and -5.68 eV which is below than the  $I^{-}/I_{3}^{-}$  redox couple (-4.6 eV vs. vacuum)<sup>29</sup> and so this favors the dye regeneration by the electrolyte.

#### **Photovoltaic Performance**

Photovoltaic properties of (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA were first investigated in devices with the basic structure of FTO/TiO<sub>2</sub>/polymer-layer/LiI/ Al. The synthesized polymers (P1-P4) were tested as a sensitizer in dye-sensitized solar cells. Typically the effective light exposure area of the DSSCs was maintained at 1 cm<sup>2</sup>, 0.05 M  $I_2/0.5$  M LiI/ 0.5 M TBAHFP solution was used as a liquid electrolyte. The photovoltaic performances of the solar cells fabricated from the prepared electrodes, under AM 1.5 solar irradiation (100 mW/cm<sup>2</sup>) are shown in Figure 6. The detailed parameters such as shortcircuit current density  $(J_{SC})$ , open-circuit voltage  $(V_{OC})$ , fill factor (FF) and overall conversion efficiency (PCE,  $\eta$ ) were summarized in Table 3. Figure 6 clearly shows the efficiency of the fabricated device decreasing on the order of (TPA-In-BzI)PMA > (Ac-In-BzI)PMA > (In-In-BzI)PMA > (Py-In-BzI)PMA. Among the polymers (P1-P4), triphenylamine and acridine donor based polymer of (TPA-In-BzI)PMA and (Ac-In-BzI)PMA show higher efficiency (3.70 and 2.81%) contributed by the high value of  $J_{SC}$ ,  $V_{OC}$  and FF compared to indole and pyrene donor based polymers (In-In-BzI)PMA and (Py-In-BzI)PMA (see Table 3). The (In-In-BzI)PMA and (Py-In-BzI)PMA polymers showed the overall conversion efficiency of 1.95 and 1.54%. In the donor segment triphenylamine and acridine rings were rich electron centre to push charge transfer in the molecule than the indole and pyrene groups, it separates the polymer in the TiO<sub>2</sub> surface which may be the reason for the higher efficiency of (TPA-In-BzI)PMA and (Ac-In-BzI)PMA polymers based solar cells.<sup>30</sup> While introducing the



**FIGURE 5** Energy diagram of the Bzl-In-chalcone containing polymers (**P1–P4**). [Color figure can be viewed at wileyonlinelibrary. com]

indole-chalcone unit in the middle of the synthesized polymers (**P1–P4**), the photo-current density ( $J_{SC}$ ) and overall current conversion efficiency were increased because the intramolecular charge transfers (ICT) effect of indole-chalcone unit.<sup>31</sup> This is due to the red-shift absorption maxima in the visible region, reduced band-gap and the LUMO levels were brought very closer to the conduction band of TiO<sub>2</sub> which favours the better electron injection to the TiO<sub>2</sub> surface under light illumination and leads to the effective charge collection. Furthermore, the **(TPA-In-BzI)PMA** device yielded an PCE of 3.70% with a  $J_{sc}$  of 8.3 mA cm<sup>-2</sup> and a  $V_{oc}$  of 0.69 V, because TPA has much better donor-capability than Ac. This is in good agreement with the absorption and IPCE spectra of these polymer-sensitizers.

The action spectra of monochromatic incident photonto-current conversion efficiency (IPCE) of **(In-In-BzI)PMA**, **(Ac-In-BzI)PMA**, **(TPA-In-BzI)PMA**, and **(Py-In-BzI)PMA** polymers fabricated DSSCs were plotted in Figure 7 and their corresponding data were shown in Table 3. Tri-phenylamine and acridine segment containing polymers **(P3** and **P2)** based devices show higher IPCE values and the onset of the IPCE



FIGURE 6 Photocurrent-voltage curves of DSSCs based on P1-P4 polymers DCM medium. [Color figure can be viewed at wileyonlinelibrary.com]

9

**TABLE 3** DSSC Performance Parameters of the Synthesized

 Polymers (P1–P4)

Polymer	J <sub>sc</sub> (mA/cm²)	$V_{\rm oc}$ (V)	FF	(η) (%)	IPCE (%)
P1	3.8	0.80	0.44	1.95	22.5
P2	6.4	0.77	0.54	2.81	24.8
P3	8.3	0.69	0.73	3.70	26.2
P4	2.8	0.77	0.82	1.54	19.5

spectra from 450 nm while compared to the polymers with indole and pyrene segment (**P1** and **P4**) based device whose onsets only from 430 nm and 390 nm. The higher IPCE led to a higher  $J_{SC}$  and in turn a higher  $\eta$  for (**TPA-In-BzI**)**PMA** and (**Ac-In-BzI**)**PMA**. By introducing the indole-chalcone group to the middle of the polymer, the former IPCE values around the maximum are higher and terminal electron rich unit indole, acridine, tri-phenylamine, and pyrene that improved the light-harvesting capability of the polymers.<sup>32</sup> The IPCE spectral study also follows the same trend as J-V measurement study. This also supports that the indole-chalcone linked nitrobenzimidazole unit containing polymers are better candidate for DSSC applications. Further studies on improving the IPCE of the chalcone-substituted metal-free polymers are currently underway.

#### **Impedance Analysis**

To further elucidate the photovoltaic properties, electrochemical impedance spectroscopy (EIS) analysis was employed to analyze interfacial charge recombination and carrier transportation processes in DSSCs based on **(In-In-BzI)PMA**, **(Ac-In-BzI)PMA**, **(TPA-In-BzI)PMA**, and **(Py-In-BzI)PMA** under dark conditions. Figure 8(a) displays the Nyquist plots, which describe the resistance of charge recombination between electrons on the TiO<sub>2</sub> conduction band and  $I_3^-$  ions in the electrolyte.<sup>33</sup> The Nyquist plots show the radius of the middle semicircle to increase in



**FIGURE 7** IPCE curves of DSSCs based on **P1–P4** polymers. [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 8** EIS spectra of DSSCs measured at 100 mW/cm<sup>2</sup>. (a) Nyquist plots. (b) Bode phase plots. [Color figure can be viewed at wileyonlinelibrary.com]

the order of (Pv-In-BzI)PMA < (In-In-BzI)PMA < (Ac-In-BzI)PMA < (TPA-In-BzI)PMA and indicating that the electron recombination resistance augments from (Py-In-BzI)PMA, (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA. In addition, the electron recombination lifetime (s) could be calculated from the Bode phase plots Figure 8(b) and electron lifetime values were 6.55, 9.22, 10.08, and 6.02 ms for (Py-In-BzI)PMA, (In-In-BzI)PMA, (Ac-In-BzI)PMA, and (TPA-In-BzI)PMA polymers, respectively. The longer electron lifetime observed with (Ac-In-BzI)PMA and (TPA-In-BzI)PMA relative to (Py-In-BzI)PMA and (In-In-BzI)PMA polymers indicated more effective suppression of the back reaction of the injected electron with the  $I^{-}/I_{3}^{-}$  in the electrolyte (Warburg diffusion) and it reflected the improvements seen in the photocurrent, yielding substantially enhanced device efficiency.<sup>34</sup> Therefore, larger the charge recombination resistance and enhanced electron lifetime might be the intrinsic reason for the higher value which can be utilized as fabric materials in optoelectronic devices (PVC) based on (Ac-In-BzI)PMA and (TPA-In-BzI)PMA polymers which have a stronger influence in tuning the energy levels but the low electron lifetime and higher electron recombination (from Fig. 8) of (Py-In-BzI)PMA, (In-In-BzI)PMA polymers might be the reason for lower performance.



#### CONCLUSIONS

In summary, four new metal-free  $\pi$ -conjugated side chain methacrylate polymers (In-In-BzI)PMA, (Ac-In-BzI)PMA, (TPA-In-BzI)PMA, and (Py-In-BzI)PMA carrying benzimidazole as acceptor and indole-chalcone unit as  $\pi$ -bridge system but with different electron donor, viz. indole, acridine, triphenylamine, and pyrene, were designed and synthesized. It can be found that the introduction of indole-chalcone unit in the middle of the polymer as  $\pi$ -bridge lead to a red-shifted absorption and charge recombination, which usually have an effect on the efficiency of the photovoltaic device. When applied to DSSCs, (TPA-In-BzI)PMA polymer based solar device (DSSCs) exhibited the power conversion efficiency of 3.70% under standard light illumination (AM 1.5G, 100 mW cm<sup>-2</sup>). Our ongoing research will focus on functionalizing tri-phenylamine based polymer-sensitizer with different substituents to modify the HOMO energy level, which will align the energy level of different polymer assemblies in the solar cell (DSSCs) and establish the charge transport more efficient.

#### ACKNOWLEDGMENTS

The authors acknowledge, Instrumentation facility provided under DST-FIST and DRS-UGC to Department of Chemistry, Anna University, Chennai and India.

#### **REFERENCES AND NOTES**

1 S. Balamurugan, S. Nithyanandan, C. Selvarasu, G. Y. Yeap, P. Kannan, *Polymer* **2012**, *53*, 4104–4111.

**2** (a) G. D. Sharma, M. Singh, R. Kurchania, E. N. Koukarascd, J. A. Mikroyannidis, *RSC Adv.* **2013**, *3*, 18821–18834; (b) S. R. Forrest, *Nature* **2004**, *428*, 911–918.

**3** (a) W. Su, Q. Fan, M. Xiao, J. Chen, P. Zhou, B. Liu, H. Tan, Y. Liu, R. Yang, W. Zhu, *Macromol. Chem. Phys.* **2014**, *215*, 2075–2083; (b) Y. Ooyama, Y. Harima, *Eur. J. Org. Chem.* **2009**, *18*, 2903–2934.

**4** P. Thongkasee, A. Thangthong, N. Janthasing, T. Sudyoadsuk, S. Namuangruk, T. Keawin, S. Jungsuttiwong, V. Promarak, *Appl. Mater. Interfaces* **2014**, *6*, 8212–8222.

**5** G. Leem, Z. A. Morseth, K. Wee, J. Jiang, M. K. Brennaman, J. M. Papanikolas, K. S. Schanze, *Chem. Asian J.* **2016**, *11*, 1257–1267.

6 (a) B. G. Kim, K. Chung, J. Kim, *Chem. Eur. J.* 2013, *19*, 5220–5230; (b) M. Liangwab, J. Chen, *Chem. Soc. Rev.* 2013, *42*, 3453.

**7** (a) A. K. Biswas, S. Barik, A. Sen, A. Das, B. Ganguly, *J. Phys. Chem. C.* **2014**, *118*, 20763–20771; (b) T. Y. Wu, M. H. Tsao, F. L. Chen, S. G. Su, C. W. Chang, H. P. Wang, Y. C. Lin, W. C. Ou-Yang, I. W. Sun, *Int. J. Mol. Sci.* **2010**, *11*, 329–353.

8 (a) M. Pannipara, A. M. Asiri, M. N. Alamry, S. A. Arshad, El-Daly, *Spectrochim. Acta Part A* 2015, *136*, 1893–1902; (b) S. Chambon, A. D'Aleo, C. Baffert, G. Wantza, F. Fages, *Chem. Commun.* 2013, *49*, 3555–3557.

**9** (a) X. Wang, J. Yang, H. Yu, F. Li, L. Fan, W. Sun, Y. Liu, Z. Y. Koh, J. Pan, W. L. Yim, L. Yan, Q. Wang, *Chem. Commun.* **2014**, *50*, 3965; (b) A. Baheti, S. R. Gajjela, P. Balaya, K. R. Justin Thomas, *Dyes Pigments* **2015**, *113*, 78–86.

**10** (a) F. Dumur, *Org. Electron.* **2015**, *25*, 345–361; (b) C. H. Chang, R. Griniene, Y. D. Su, C. C. Yeh, H. C. Kao, J. V.

Grazulevicius, D. Volyniuk, S. Grigalevicius, *Dyes Pigments* **2015**, *122*, 257–263.

**11** W. Yuan, H. Zhao, H. Hu, S. Wang, G. L. Baker, *ACS Appl. Mater. Interfaces* **2013**, *5*, 4155–4161.

**12** D. T. Nannapaneni, V. S. S. I. Gupta Atyam, M. I. Reddy, C. H. Sarva Raidu, *J. Young Pharm.* **2010**, *2*, 273–279.

**13** P. Rajakumar, N. Venkatesan, G. Mohanraj, *RSC Adv.* **2014**, *4*, 21190–21194.

**14** S. Selvam, S. Nanjundan, *React. Funct. Polym.* **2005**, *62*, 179–193.

**15** R. Baskar, K. Subramanian, *Spectrochim. Acta Part A* **2011**, *79*, 1992–1997.

16 S. J. Santhosh Kumar, K. Subramanian, J. Polym. Mater. Polym. Biomater. 2013, 62, 627–634.

17 Q. Wang, S. Ito, M. Gratzel, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, J. Phys. Chem. B 2006, 110, 25210–25221.

**18** H. J. Ahn, S. Thogiti, J. M. Cho, B. Y. Jang, J. H. Kim, *Electron. Mater. Lett.* **2015**, *11*, 822–827.

19 A. Rehab, N. Salahuddin, Polymer 1999, 40, 2197-2207.

**20** A. V. Rami Reddy, K. Subramanian, V. Krishnasamy, J. Ravichandran, *Eur. Polym. J.* **1996**, *32*, 919–926.

**21** C. Zafer, B. Gultekin, C. Ozsoy, C. Tozlu, B. Aydin, J. Icli, *Solar Energy Mater. Solar Cells* **2010**, *94*, 655–661.

22 S. Kumar, K. R. Justin Thomas, C. T. Li, K. C. Ho, *Org. Electron.* 2015, *26*, 109–116.

**23** H. Jiang, K. Oniwa, A. Islam, J. Zhao, L. Han, Y. J. Sun, M. Bao, N. Asao, Y. Yamamoto, T. Jin, *Tetrahedron* **2015**, *71*, 6534–6540.

**24** (a) D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* **2007**, *72*, 9550–9556; (b)W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, *J. Phys. Chem. C* **2008**, *112*, 874–880; (c) T. Duana, K. Fan, T. Peng, C. Zhong, Y. Hea, X. Chen, *Synth. Met.* **2016**, *211*, 19–24.

**25** (a) S. Manoharan, S. Anandan, *Dyes Pigments* **2014**, *105*, 223–231; (b) X. Zang, Z. Huang, H. Wu, Z. Iqbal, L. Wang, H. Meier, D. Cao, *J. Power Sources* **2014**, *271*, 455–464.

26 M. Lim, K. Song, Y. Kang, J. Ko. Dyes Pigments 2015, 119, 41–48.

27 S. Erten, E. Eren, S. Icli. J. Appl. Phys. 2007, 38, 227-230.

**28** T. Chih-Hung, L. Chun-Yang, C. Ming-Che, H. Tsung-Wei, W. Chung-Chih, C. Yi-Wen, *Org. Electron.* **2013**, *14*, 3131–3137.

29 P. Rajakumar, K. Visalakshi, S. Ganesan, P. Maruthamuthu, S. A. Suthanthiraraj, *J. Mater. Sci.* 2012, *47*, 1811–1818. [Cross-Ref][10.1007/s10853-011-5967-9][Mismatch

**30** (a) H. Yang, M. Huang, J. Wu, Z. Lan, S. Hao, J. Lin, *Mater. Chem. Phys.* **2008**, *110*, 38–42; (b) M. Imperiyka, A. Ahmad, S. Abu-Hanifah, A. Ali-Umar, N. Sabirin Mohamed, M. Y. A. Rahman, *J. Polym. Eng.* **2014**, *34*, 695–702; (c) E. Puodziukynaite, H. W. Wang, J. Lawrence, A. J. Wise, T. P. Russell, M. D. Barnes, T. Emrick, *J. Am. Chem. Soc.* **2014**, *136*, 11043–11049.

**31** S. Ramkumar, S. Manoharan, S. Anandan, *Dyes Pigments* **2012**, *94*, 503–511.

**32** (a) C. L. Chochos, S. A. Choulis, *Prog. Polym. Sci.* **2011**, *36*, 1326–1414; (b) X. Liu, Z. Cao, H. Huang, X. Liu, Y. Tan, H. Chen, Y. Pei, S. Tan, *J. Power Sources* **2014**, *248*, 400–406.

**33** Z. S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, F. Furube, K. Hara, *Chem. Mater.* **2008**, *20*, 3993–4003.

**34** L. L. Tan, H. Y. Chen, L. F. Hao, Y. Shen, L. M. Xiao, J. M. Liu, D. P. Kuanga, C. Y. Su, *Chem. Phys.* **2013**, *15*, 11909.

