High-Performance ZnPc Thin Film-Based Photosensitive Organic Field-Effect Transistors: Influence of Multilayer Dielectric Systems and Thin Film Growth Structure

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Supporting Information

ABSTRACT: The key impact and significance of a multilayer polymer-based dielectric system on the remarkable photoresponse properties of zinc phthalocyanine (ZnPc)-based photosensitive field-effect transistors (PS-OFETs) have been systematically analyzed at various incident optical powers. A combination of inorganic aluminum oxide (Al₂O₃) and organic nonpolar poly(methyl methacrylate) (PMMA) is used as the bilayer dielectric configuration, whereas in the trilayer dielectric system, a bilayer polymer dielectric, consisting of PMMA, as the low-k dielectric polymer, on top of poly(vinyl alcohol) (PVA), the high-k polar dielectric, has been fabricated along with Al₂O₃ as the third layer. Before fabricating the OFETs, a systematic optimization of the nature of growth of the ZnPc molecules, deposited on PMMA-coated glass substrates at different substrate temperatures (Tₛ) was performed and examined by atomic-force microscopy, field-emission scanning electron microscopy, X-ray diffraction, and Raman analysis. At 90 °C, the fabricated PS-OFETs with the Al₂O₃/PVA/PMMA trilayer dielectric configuration showed the best p-channel behavior, with an enhanced and remarkable photoresponsivity of R ~ 9689.39 A W⁻¹ compared to that of the Al₂O₃/PMMA bilayer dielectric system (R ~ 2679.40 A W⁻¹) due to the polarization of the dipoles inside the polar PVA dielectric, which increases the charge transport through the channel. The charge carrier mobility of the device also improved by one order (μₑ ≈ 1.3 × 10⁻⁵ cm² V⁻¹ s⁻¹) compared to that of the bilayer dielectric configuration (μₑ ~ 3.5 × 10⁻⁴ cm² V⁻¹ s⁻¹). The observed specific detectivity (D*) and NEP values of the bilayer dielectric system were 6.01 × 10¹³ Jones and 2.655 × 10⁻¹⁷ W Hz⁻¹/₂, whereas for the trilayer dielectric system, the observed D* and NEP values were 5.13 × 10¹⁴ Jones and 1.043 × 10⁻¹⁷ W Hz⁻¹/₂, respectively. Additionally, the operating voltage of each of the fabricated devices was also very low (−10 V) due to the influence of the inorganic high-k Al₂O₃ dielectric layer. The electrical stability of all of the fabricated devices was also investigated by bias stress analysis under both light and dark conditions in vacuum. To the best of our knowledge, the photoresponsivity (R) reported here with an Al₂O₃/PVA/PMMA trilayer dielectric configuration is the highest reported value for thin film-based PS-OFETs, at a remarkably low operating voltage of −10 V, on low-cost glass substrates without indium tin oxide or/and Si/SiO₂.

INTRODUCTION

Investigation of highly efficient organic optical sensors is one of the most promising research topics due to their potential applications in various optoelectronic devices as low-cost active optoelectronic components compared with their conventional inorganic counterparts.²,³ Although the widely used optical sensors, such as photodiodes, charge-coupled devices, and so forth, consisting of inorganic active materials show promising sensitivity, their high fabrication cost, high power consumption, and poor flexibility have reduced their demand in new-generation wearable and flexible electronics.¹ Thus, for practical applications, it is vital that an ideal optical sensor should have a low operating voltage, high photoresponsivity, and high optical and electrical stability and that it should be low in cost and versatile in fabrication on the desired substrate, preferably using economical solution-based techniques. In this regard, organic π-conjugated semiconductor-based photosensitive organic field-effect transistors (PS-OFETs) offer numerous advantages, including their unique ability to detect light; low noise; switching capability; signal magnification in a single, low-cost manufacturing; and flexible device configuration.¹⁵ PS-OFETs is a three-terminal photosensitive organic electronic component, in which photogenerated excitons at the active channel can easily be dissociated through the applied gate bias, which provides highly effective and magnified photodetection. However, for the fabrication of highly photoresponsive/sensitive OFETs, several factors have to be considered: (i) the active material should have a high and broad absorption spectrum so that maximum number of carriers can be generated by the incident light, (ii) the mobility of the active material...
should be superior to obtain easy transportation of the photogenerated charge carrier through the channel, and (iii) the energy barrier between the active material and electrodes should be as low as possible so that the charge carriers can be collected for signal efficiently.\(^6\) Generally point (i) can be improved through different chemical syntheses protocols by modulating the chemical structure of the active material. However, the low mobility of most organic semiconductors constrains the fulfillment of points (ii) and (iii). Herein, by introducing multilayer dielectric systems and tuning the thin-film morphology of the active layer material at different substrate temperature \((T_s)\), process (ii) was modified to realize vital improvements in the PS-OFET performance. Among organic semiconductors, porphyrins and phthalocyanines are two representative macrocyclic systems that are used as active materials in PS-OFETs due to their wide range of optical absorption spectra and easily tunable electrical and optical properties, by which one can modify their thin film growth microstructures.\(^7,8\) Because the dielectric–active material interface and molecular packing of the active layer have a strong influence on the mobility of OFETs, it is very important to utilize sustainable materials, such as polymers, and clearly understand the growth mechanism of these polymer-based dielectric layers in the device to optimize the thin film growth structure of the deposited active layer prior to device fabrication.\(^9\)

Hence, the impact of the thin film growth structure and multilayer polymer dielectric systems on the photoresponse properties of zinc phthalocyanine (ZnPc)-based PS-OFETs at various incident optical powers has been systematically analyzed. A combination of inorganic aluminium oxide \((\text{Al}_2\text{O}_3)\) and organic nonpolar poly(methyl methacrylate) \((\text{PMMA})\) is used as the bilayer dielectric configuration, whereas in the trilayer dielectric system, the bilayer polymer dielectric, consisting of PMMA as the low-\(k\) dielectric polymer, on the top poly(vinyl alcohol) \((\text{PVA})\), the high-\(k\) polar dielectric, is used along with \(\text{Al}_2\text{O}_3\) as the third layer. The growth nature of the ZnPc molecules deposited on PMMA-coated glass substrates at different substrate temperatures \((T_s)\), that is, at room temperature \((\text{RT})\) and 60, 90, and 120 \(^\circ\text{C}\), respectively, was systematically analyzed by various characterization techniques, such as atomic-force microscopy \((\text{AFM})\), field-emission scanning electron microscopy \((\text{FESEM})\), X-ray diffraction \((\text{XRD})\), and Raman analysis, to optimize \(T_s\) for the best device performance. At 90 \(^\circ\text{C}\), the fabricated PS-OFETs with the \(\text{Al}_2\text{O}_3/\text{PVA}/\text{PMMA}\) trilayer dielectric configuration showed the best p-channel behavior, with an enhanced and remarkable photoresponsivity of \(R \sim 9689.39 \text{ A W}^{-1}\) compared to that of the \(\text{Al}_2\text{O}_3/\text{PMMA}\) bilayer dielectric system \((R \sim 2679.40 \text{ A W}^{-1})\) because of superior charge transport through the channel by polarization of the dipoles inside the polar PVA dielectric, which increases the charge carrier mobility by one order \((\mu_h \sim 1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) compared to that of the bilayer dielectric configuration \((\mu_h \sim 3.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\). The observed specific detectivity \((D^*\text{)}\) and noise equivalent power \((\text{NEP})\) values of the bilayer dielectric system were \(6.01 \times 10^{13} \text{ Jones}\) and \(2.655 \times 10^{-17} \text{ W Hz}^{-1/2}\), whereas for the trilayer dielectric system, the observed \(D^*\) and NEP values were \(5.13 \times 10^{14} \text{ Jones}\) and \(1.043 \times 10^{-17} \text{ W Hz}^{-1/2}\), respectively. Additionally, the operating voltages of each of the fabricated devices were observed to be exceedingly low \((-10 \text{ V})\) due to the influence of the inorganic high-\(k\) \(\text{Al}_2\text{O}_3\) dielectric layer. The electrical stability of each of the fabricated devices was also investigated by bias stress analysis under both light and dark conditions in vacuum. To the best of our knowledge, the photoresponsivity, \(R\), reported herein with the \(\text{Al}_2\text{O}_3/\text{PVA}/\text{PMMA}\)
PMMA trilayer dielectric configuration is the highest value among that of all of the thin film-based PS-OFETs, with a remarkably low operating voltage of ∼10 V. This result suggests that the Al₂O₃/PVA/PMMA configuration along with an appropriate Tₜ for ZnPc deposition generates highly efficient ITO and Si/SiO₂-free devices, with benchmark photoresponsivity performances of PS-OFETs, which are expected to have potential applications in future low-cost and wearable optoelectronic devices.

## RESULTS AND DISCUSSION

### Thin Film Growth Structure and Surface Analysis

The growth structure and thin-film morphology of thermally deposited ZnPc molecules at Tₛ = 90 °C on PMMA-coated glass substrates along with their respective root-mean-square roughnesses (σ rms) is shown in Figure 1. At 90 °C, the AFM and FESEM images of the ZnPc thin film (Figure 1a,b) showed continuous and uniform fiberlike crystallinity, with a very low σ rms of ∼3.43 nm compared to that of films deposited at other temperatures (see Figures S1 and S2). This observation was also supported by the XRD and Raman analyses (see Figure 1c,d). It was observed that the XRD spectra of ZnPc molecules at 90 °C showed the highest particle size, D = 22.74 nm and a d-spacing value of 12.74 Å at 2θ = 6.93°. The calculated d-spacings of all of the thin films deposited at different Tₛ along with their respective peak positions are summarized in Table S1 and Figure S3. From the Raman spectra (see Figure S4), it was observed that up to Tₛ = 90 °C the integral intensities of the 1341 and 1512 cm⁻¹ modes, which are generally responsible for the stretching and bending vibrations of the Zn and N interaction, increased systematically and thereafter they started showing anomalous behavior for both 1341 and 1512 cm⁻¹ (see Figure S5a,b). However, in the case of full width at half-maximum (see Figure S5c,d), a systematic increase in behavior was observed from RT to 120 °C.

This observed anomaly in the integral intensity modes indicates that there is a change in the planarity of the thin film growth pattern of ZnPc molecules due to the deformation in the symmetry of the molecular structure, which is initiated at Tₛ = 90 °C because of the interaction of the heavy Zn atom with nitrogen, indicating that Tₛ has a strong influence on the growth structure of ZnPc molecules and 90 °C is the optimum Tₛ for ZnPc-OFET fabrication. The bandgap of the ZnPc molecules at 90 °C, estimated from the Q-band first peak maxima (at 624 nm) (inset of Figure 1c) is ∼1.97 eV, whereas for the second maxima (699 nm), it is ∼1.77 eV, which indicates that ZnPc could be easily excited and be responsive to visible light. The details of all of the experimental observations are given in the Supporting Information (Figures S1–S5).

### Device Fabrication and Characterization

ZnPc-based PS-OFETs were fabricated on bilayer (Al₂O₃/PMMA) and trilayer (Al₂O₃/PVA/PMMA) dielectric systems with a bottom-gate top-contact configuration. Schematic representations are shown in the Operational Mechanism section. Generally, for low-voltage operation and reduced power consumption, high-k dielectrics are used in the case of OFET fabrics. There are several high-k inorganic dielectric materials that are used in OFETs, such as Al₂O₃, which is one of the most promising materials because of its excellent insulating properties and low-cost deposition process. In this study, Al₂O₃ is used as the high-k inorganic dielectric layer for low-voltage operation, which is deposited by the anodic oxidation method, with a constant current density of 0.06 mA cm⁻² and a 0.001 M citric acid monohydrate electrolyte solution, followed by the procedure mentioned in the earlier report.

Citric acid was used for the deposition of barrier-type Al₂O₃ to reduce the leakage current problem of the anodized inorganic dielectric layer. Because the grown Al₂O₃ thin film inherently has a very high surface roughness (σ rms ~ 11.22 nm), a 100 nm PMMA (30 mg mL⁻¹ in anisole) film was spun on top of the Al₂O₃ layer and dried for 1 h at 100 °C under an
inert atmosphere to obtain a smooth surface ($\sigma_{\text{rms}} \sim 1.97$ nm) (see Figure S6).

However, in the case of the Al$_2$O$_3$/PMMA bilayer dielectric system, although the devices were highly stable and hysteresis-
free, the drain current was less and charge transportation through the channel was poor. Hence, a high-k polar PVA dielectric was inserted in between PMMA and Al2O3 layers so that the polar PVA dielectric could induce more charges into the channel, and further, the nonpolar PMMA dielectric would prevent direct interaction of the –OH groups of the polar PVA dielectric layer with the active layer molecules. As a result, enhancement of the drain current, with superior device stability, could be achieved simultaneously. The capacitance densities (C0) of the Al2O3/PMMA and Al2O3/PVA/PMMA gate insulators were calculated independently from the metal–insulator–metal structure of a parallel-plate capacitor, using copper as the top electrode (see Figure S7). After the deposition of gate dielectric layers, a 60 nm (±10 nm) ZnPc active material was deposited by thermal deposition under a base pressure of 10−6 mbar at T = 90 °C. Further, Cu source–drain electrodes were thermally deposited at RT (∼80 nm) to calculate the three terminal properties of the PS-OFETs.

The photoresponse characteristics of ZnPc-based PS-OFETs with Al2O3/PMMA and Al2O3/PVA/PMMA gate dielectric configurations under various incident optical power illuminations are shown in Figure 2. The typical channel length (L) and channel width (W) of the devices were kept at 40 and 780 µm, respectively. Figure 2a,c represents the drain characteristics of the devices with bilayer and trilayer device configurations illuminated with the lowest optical power (P in = 0.002 W m−2), whereas Figure 2b,d represents the shift in the threshold voltage in the transfer characteristic curve of the devices under irradiation with various optical powers. From these drain and transfer characteristics, it could be concluded that the device with the Al2O3/PVA/PMMA configuration showed a significant increase in the drain current with a low operating voltage under illumination with light compared to that of the Al2O3/PMMA configuration due to the slow polarization of the dipole in vacuum present at the high-k PVA dielectric that induced more charges at the semiconducting channel of the PS-OFETs. The photoresponsivity (R) of the device was calculated by using eq 1

$$R = \frac{I_{ph}}{P_{opt}} = \frac{(I_{DS,illuminated} - I_{DS, dark})}{P_{in}}$$

where I ph represents the source-to-drain photocurrent; P opt is the incident light power; I DS,dark and I DS,illuminated are the source–drain current under dark and illumination conditions; and P in represents the power of the incident light per unit area, respectively. S is the effective sensing area of the device.

It was observed that the Al2O3/PVA/PMMA devices showed remarkable photoresponsive behavior, R ≈ 9689.39 A W−1, at V DS = −7 V and V GS = −8 V under illumination with a very low optical power, P in = 0.002 W m−2, over a small effective sensing area, S = 2.54 × 10−8 cm2. The photo ON/OFF current ratio of the same device is observed to be 5.8 under illumination with the highest optical power, P in = 0.2957 W m−2, with the same biasing condition. Moreover, the operating voltage of the device was also incredibly low (∼10 V), confirming the consumption of very less electrical power to operate this device. The graphical representation of IDS versus VGS and the photocurrent and responsivity curves for different incident powers and VGS values for both the dielectric configurations are shown in Figures S8 and S9. All device parameters of the ZnPc-based PS-OFETs in the dark and under various optical power illuminations with the Al2O3/PMMA and Al2O3/PVA/PMMA dielectric configurations are summarized in Table 1.

**Operational Mechanism.** Figure 3 schematically represents the operation mechanism of ZnPc-based PS-OFETs under dark and light illumination conditions, with (Figure 3a–f) Al2O3/PMMA bilayer and (Figure 3g–l) Al2O3/PVA/PMMA trilayer device configurations, respectively. The voltage applied between the source and drain and the gate and source are represented by V DS and V GS, respectively. As the devices were fabricated in a bottom-gate top-contact configuration, the amount of current flow from the source to the drain contacts through the ZnPc thin film and is strongly dependent on the amount of gate voltage, V GS applied through the gate electrode for a particular V DS. Because the semiconducting layer and gate electrode are capacitively coupled with each other through the multilayer dielectric system, the charges induced in the semiconducting thin film are generally mobile charges and move in response to the particular V DS.

Figure 3a,g represents the general schematic of the two different device configurations, namely, Al2O3/PMMA and Al2O3/PVA/PMMA. Under the dark condition, when V DS = V GS = 0 V (see Figure 3b,h), both the devices are in the “OFF” state because no current flows from the source to the drain contacts. Under this equilibrium condition, when light is illuminated onto the channel with a minimum threshold power (Figure 3c,i), excitons are formed in the semiconducting layer. However, as V DS = V GS = 0 V, there is no current flow from the source to the drain and only the photogenerated charge carriers are present in the semiconductor layer. When V DS < 0 V and V GS = 0 V (Figure 3d,j), positively charged holes, initially present in the p-type ZnPc semiconductor, start moving toward the negatively biased drain contact.

At the same time, the photogenerated excitons begin to dissociate due to the applied V DS and increase the positive charge carrier concentration at the channel. Because there are no mobile charges present under this condition (as V GS = 0 V), the total current between the source and drain is negligible at this stage. When the gate voltage is applied, that is, V DS < 0 V and V GS < 0 V, in the case of the Al2O3/PMMA device configuration (Figure 3e), mobile charges are induced in the ZnPc semiconductor thin film through the bilayer dielectric system and the transistor comes to its “ON” state. These mobile charges create a large electric field at the semiconductor–dielectric interface, which shift the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the semiconductor upward to match the HOMO to the Fermi level of the copper drain contact. Because V DS is already less than 0 V under this condition, more positively charged holes will flow through the channel, thereby increasing the drain current. Moreover, the additional holes present in the channel due to the light illumination further enhances the drain current in the presence of light compared to that in the dark. When the gate voltage decreases from a more negative value to a less negative value (i.e., gate voltage sweeps from −10 to 0 V) under the same conditions, that is, V DS < 0 V and V GS < 0 V (Figure 3f), the concentration of mobile charges starts to decrease immediately at the PMMA–semiconductor thin-film interface, which further shifts the HOMO and LUMO levels of the semiconductor downward to the Fermi level of the copper drain contact. As a result, the current starts to decrease.

As PMMA is a nonpolar polymer dielectric, trapping of charges at the semiconductor–dielectric interface becomes less, which is also proven by hysteresis analysis (Figure 4b). A similar...
phenomenon also takes place in the case of the Al\textsubscript{2}O\textsubscript{3}/PVA/PMMA trilayer dielectric configuration. The nonpolar PMMA dielectric layer was used here on top of the polar PVA dielectric to prevent direct contact of the polar —OH groups in the PVA dielectric with the semiconductor thin film so that trapping of the charges becomes less at the PMMA—ZnPc interface compared to that at the PVA—ZnPc interface. PVA is a high-

\( k \) dielectric polymer containing polar —OH groups that are randomly distributed when \( V_{\text{GS}} = 0 \) V. When the gate voltage is applied, that is, \( V_{\text{DS}} < 0 \) V and \( V_{\text{GS}} < 0 \) V (Figure 3k), these —OH groups present at the PVA layer start polarizing slowly, and at maximum \( V_{\text{GS}} \), almost all of the groups are fully polarized. These polarized —OH groups generate an additional electric field at the PVA and PMMA dielectric interface, which can further help induce more mobile charges at the PMMA—semiconductor thin-film interface. These induced mobile charges along with the photogenerated charges further increase the concentration of holes at the channel. As a result, the drain current becomes higher under this condition compared to that in the bilayer dielectric configuration (Figure 3e). When the gate voltage decreases from a more negative value to a less negative value, as in the bilayer dielectric system under the same condition, that is, \( V_{\text{DS}} < 0 \) V and \( V_{\text{GS}} < 0 \) V (Figure 3l), the same mechanism as that in Figure 3f is expected to take place. However, because of the slow polarization of the hydroxyl group at the PVA dielectric, the polarity of the electric field at the PVA—PMMA changes very slowly. As a result, although \( V_{\text{GS}} \) sweeps from \(-10\) to \( 0 \) V, at this stage, some positively polarized mobile charges remain at the PMMA—semiconductor thin-film interface, which oppose the sudden decay of the drain current, resulting in a hysteresis of the transfer characteristics (Figure 4d).

Further, to study the operational stability of both the fabricated bilayer and trilayer PS-OFTs, the time-dependent decay of \( I_{\text{DS}} \) in dark and light conditions under direct current (DC) bias stress at \( V_{\text{DS}} = -7 \) V and \( V_{\text{GS}} = -8 \) V over 1200 s was recorded (Figure 4a,b). It was observed that the decay of drain current in the Al\textsubscript{2}O\textsubscript{3}/PMMA device configuration was very slow compared to that in Al\textsubscript{2}O\textsubscript{3}/PVA/PMMA due to lesser trapping of charges at the dielectric—semiconductor interface. Additionally, for Al\textsubscript{2}O\textsubscript{3}/PVA/PMMA, an anomalous bias stress effect was observed due to slow polarization of the hydroxyl group. Moreover, although in both dielectric configurations the charge trap density increases (Table 1) in the presence of light illumination compared to that in dark, in the bias stress study, lesser decay of \( I_{\text{DS}} \) was observed in the presence of light compared to that in dark because of the higher \( I_{\text{DS}} \) values in the presence of light at \( V_{\text{GS}} = -8 \) V and \( V_{\text{DS}} = -7 \) V. This is because electron—hole pairs are generated in the organic semiconductor after illumination. The excited electrons are transferred from the HOMO to the LUMO level. As a result, we observed enhancement in the drain current in the presence of light illumination.

To analyze the relaxation characteristics of both the fabricated devices, their rise and decay responses were fitted with eqs 2 and 3 (see Figure S10) to estimate the growth and decay processes of \( I_{\text{DS}} \):

\[
I_{\text{light growth}} = I_{\text{DS,dark}} + A \exp \left[ \frac{-t}{\tau_1} \right] + B \exp \left[ \frac{-t}{\tau_2} \right] \tag{2}
\]

\[
I_{\text{light decay}} = I_{\text{DS,dark}} + A \exp \left[ \frac{-t}{\tau_1} \right] + B \exp \left[ \frac{-t}{\tau_2} \right] \tag{3}
\]

where \( I_{\text{DS,dark}} \) is the dark current, \( A \) and \( B \) are the scaling constants, \( t \) is the time when the light was turned ON or OFF, and \( \tau_1 \) and \( \tau_2 \) are the time constants. Time constant \( \tau_1 \) represents the carrier generation and recombination processes in the semiconductor thin film, and \( \tau_2 \) is related to the hole-trapping and -release processes at the interface.

In these ZnPc-based PS-OFTs with the Al\textsubscript{2}O\textsubscript{3}/PMMA bilayer dielectric system, the estimated time constants, \( \tau_1 \) and
\(\tau_d\) and \(\tau_r\) were observed to be 0.98 and 9.59 s for the decay and 0.43 s for the growth process, respectively. For the Al\(_2\)O\(_3\)/PVA/PMMA trilayer dielectric system, the estimated \(\tau_d\) and \(\tau_r\) for the decay process were observed to be 0.87 and 5.95 s and for the growth process both \(\tau_d\) and \(\tau_r\) were 0.43 s, respectively. From all of these experimental data, it is clear that the required time for carrier generation and recombination in the semiconductor thin film for both the dielectric systems is almost similar, whereas the time required for the hole trapping and release processes at the interface is much lower for the trilayer dielectric system compared to that for the Al\(_2\)O\(_3\)/PMMA bilayer system.

Generally, for an ideal optical sensor it is necessary that the device should be cost-effective, stable, and operated under a low operating voltage so that less electrical power is required during device operation. Most of the remarkable organic optical sensors reported until date are generally fabricated on Si/SiO\(_2\)-device should be cost-e-
bilayer system. growth process both decay process were observed to be 0.87 and 5.95 s and for the PMMA trilayer dielectric system, the estimated 

In this regard, a highly photoresponsive ZnPc nanobelt-based light-sensing OFET on an octadeclylchlororosilane-modified Si/SiO\(_2\) substrate with gold (Au) as the top source-drain contact was reported.\(^{16}\) Similarly, CuPc/pentacene-based PS-OFETs deposited on an Si/SiO\(_2\) substrate showed photoresponses of 0.5–2 and 10–50 A W\(^{-1}\) and a maximum photo ON/OFF current ratio of 3000 and 1.3 \(\times\) 10\(^5\), respectively, under 365 nm UV light.\(^{17}\) However, due to the extensive use of either ITO or Si/SiO\(_2\) substrates, all of these devices had a very high operating voltage that increased the external electrical power requirement to operate the device.

In this study, the significant influence of the thin film growth structure and trilayer polymer dielectric system on the highest photoresponse properties of ZnPc-based PS-OFETs at various incident optical powers is reported. At 90 °C, the PS-OFETs with the Al\(_2\)O\(_3\)/PVA/PMMA configuration showed the best p-channel behavior, with an enhanced and remarkable photo-

\[R \sim 9689.39 \text{ A W}^{-1}\]

for the Al\(_2\)O\(_3\)/PMMA bilayer dielectric system (\(R \sim 2679.40 \text{ A W}^{-1}\)) due to superior charge transport through the channel by the polarization of dipoles inside the polar PVA dielectric, which increases the charge carrier mobility, which is one order higher \((\mu_h \sim 1.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) compared to that of the bilayer dielectric configuration \((\mu_h \sim 3.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\). The observed specific detectivity, \(D^*\), and NEP [where \(D^* = R \lambda h / (2eI_{P,\text{dark}})^{1/2}\) and \(\text{NEP} = (2eI_{P,\text{dark}})^{1/2}R^{-1}\); \(e\) is the value of the electron charge] values of the bilayer dielectric system are 6.01 \(\times\) 10\(^{13}\) Jones and 2.655 \(\times\) 10\(^{-17}\) W Hz\(^{-1/2}\), whereas those for the trilayer dielectric system are 5.13 \(\times\) 10\(^{12}\) Jones and 1.043 \(\times\) 10\(^{-17}\) W Hz\(^{-1/2}\), respectively. Additionally, the operating voltages of each of the fabricated devices were observed to be very low (\(-10\) V) due to the influence of the inorganic high-k Al\(_2\)O\(_3\) dielectric layer. The electrical stability of each of the fabricated devices was also investigated by bias stress analysis under both light and dark conditions in vacuum. To the best of our knowledge, the photoresponsivity, \(R\), reported here in the case of the Al\(_2\)O\(_3\)/PVA/PMMA trilayer dielectric configuration is the highest among that of all of the thin film-based PS-OFETs, with a remarkably low operating voltage of \(-10\) V. This Al\(_2\)O\(_3\)/PVA/PMMA device with an ITO- and Si/SiO\(_2\)-free system displayed PS-OFETs with very high photoresponsivity at a low operating voltage and is expected to open newer avenues in the field of electronic devices, energy-efficient sensors, and future low-cost wearable optoelectronic devices.

### CONCLUSIONS

We have successfully reported a “thin film-based OFET” with the highest photosensitivity. This was achieved by utilizing multilayered polymer-based dielectric systems and optimizing the impact of thin film growth structure to obtain superior photoresponse properties of ZnPc-based PS-OFETs at various incident optical powers. It has been established that the thermally evaporated ZnPc films at 90 °C on PMMA thin film-coated glass substrates at different substrate temperatures exhibit a polycrystalline nature, as evident from AFM, FESEM, XRD, and Raman analysis. At 90 °C, the fabricated PS-OFETs with the Al\(_2\)O\(_3\)/PVA/PMMA trilayer dielectric configuration showed a p-channel behavior, with an enhanced and remarkable photoresponsivity of \(R \sim 9689.39 \text{ A W}^{-1}\), whereas the Al\(_2\)O\(_3\)/PMMA bilayer dielectric system showed a photoresponsivity of \(R \sim 2679.40 \text{ A W}^{-1}\). This was because of superior charge transport through the channel by the polarization of the dipoles inside the polar PVA dielectric. Overall, this increases the charge carrier mobility by one order \((\mu_h \sim 1.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) compared to that of the bilayer dielectric configuration \((\mu_h \sim 3.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\), with a very low operating voltage \((-10\) V) due to the influence of the inorganic high-k Al\(_2\)O\(_3\) dielectric layer. The electrical stability of each of the fabricated devices was also investigated by bias stress analysis under both light and dark conditions in vacuum.

### EXPERIMENTAL SECTION

**Chemicals.** ZnPc (99.9999% purity), PMMA \((M_w = 550 000 \text{ kg mol}^{-1})\), aluminum wire (99.9999% purity), and copper wire (99.9% purity) were purchased from Sigma Aldrich. Anisole (99% purity) and PVA \((M_w \sim 115 000)\) were purchased from Loba Chemie. All chemicals and materials were used as received, unless otherwise mentioned. Microscope glass slides (thickness \(\sim 1.2\) mm), purchased from Jain Scientific Glass Works, India, were used as the device substrate without any surface modification.

**Characterization Details.** The thin films of ZnPc were deposited by the thermal evaporation technique under \(10^{-6}\) mbar pressure. The thicknesses of the thin films were measured by a Veeco Dektak 150 Surface Profilometer. A Perkin-Elmer Lambda 25 UV–vis spectrophotometer was used to record the UV–vis absorption spectra. AFM images of the thin films were recorded on an Agilent 5500-STM instrument. Raman spectra were recorded on an HR 800 Raman Spectrometer. Electrochemical measurements were performed using a CH Instrument. The thin-film XRD pattern was recorded on a Rigaku TTRAX III, with Cu K\(_\alpha\) radiation. For PS-OFET measurements, white-light (quartz halogen lamp) irradiation was performed with an Oriel DC regulated illuminator connected with Lake Shore fiber optic probes having a core diameter \(\sim 18\)
μm. The optical power of the illuminated light was measured by both the Tenmars TM-207 power meter and Newport optical power/energy meter (Model 842-PE). The optoelectrical properties of all three terminals were characterized using a Keithley 4200 semiconductor characterization system with a Lake Shore vacuum probe station and Keithley 2400 source meter.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00094.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Askim, J. R.; Mahmoudi, M.; Sulsick, K. S. Optical Sensor Arrays for Chemical Sensing: The Optoelectronic Nose. *Chem. Soc. Rev.* 2013, 42, 8649–8682.

(2) Bilro, L.; Alberto, N.; Pinto, J. L.; Nogueira, R. Optical Sensors Based on Plastic Fibers. *Sensors* 2012, 12, 12184–12207.

(3) Gomes, H. L.; Stalllinga, P.; Dinelli, F.; Murgia, M.; Biscarini, F.; de Leeuw, D. M.; Muck, T.; Geurts, J.; Molenkamp, L. W.; Wagner, V. Bias-induced Threshold Voltages Shifts in Thin-Film Organic Transistors. *Appl. Phys. Lett.* 2004, 84, 3184–3186.

(4) Stalllinga, P.; Gomes, H. L.; Biscarini, F.; Murgia, M.; de Leeuw, D. M. Electronic Transport in Field-Effect Transistors of Sexithiophene. *J. Appl. Phys.* 2004, 96, 5277–5283.

(5) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. Temperature-independent Transport in High-Mobility Pentacene Transistors. *Appl. Phys. Lett.* 1998, 72, 1854–1856.

(6) Dong, H.; Bo, Z.; Hu, W. High Performance Phototransistors of a Planar Conjugated Copolymer. *Macromol. Rapid Commun.* 2011, 32, 649–653.

(7) Umeyama, T.; Takamatsu, T.; Tezuka, N.; Matano, Y.; Araki, Y.; Wada, T.; Yoshikawa, O.; Sagawa, T.; Yoshikawa, S.; Imahori, H. Synthesis and Photophysical and Photovoltaic Properties of Porphyrin-Furan and -Thiophene Alternating Copolymers. *J. Phys. Chem. C* 2009, 113, 10798–10806.

(8) Senthilarasu, S.; Hahn, Y. B.; Lee, S.-H. Structural Analysis of Zinc Phthalocyanine (ZnPc) Thin Films: X-Ray Diffraction Study. *J. Appl. Phys.* 2007, 102, No. 043512.

(9) Dong, H.; Wang, C.; Hu, W. High Performance Organic Semiconductors for Field-Effect Transistors. *Chem. Commun.* 2010, 46, S211–S222.

(10) Tackley, D. R.; Dent, G.; Smith, W. E. IR and Raman Assignments for Zinc Phthalocyanine from DFT Calculations. *Phys. Chem. Chem. Phys.* 2000, 2, 3949–3955.

(11) Basova, T. V.; Kolesov, B. A. Raman Polarization Studies of the Orientation of Molecular Thin Films. *Thin Solid Films* 1998, 325, 140–144.

(12) Cho, S. W.; Jeong, J. G.; Park, S. H. J.; Cho, M.-H.; Jeong, K.; Whang, C.-N.; Yi, Y. The Characteristics and Interfacial Electronic Structures of Organic Thin Film Transistor Devices with Ultrathin (Hf O 0.7(Si O 2)n) Gate Dielectrics. *Appl. Phys. Lett.* 2008, 92, No. 213302.

(13) Majewski, L. A.; Schroeder, R.; Grell, M. One Volt Transistor. *Adv. Mater.* 2005, 17, 192–196.

(14) Koo, J. B.; Ku, C. H.; Lim, C.; Kim, S. H.; Lee, J. H. Hysteresis and Threshold Voltage Shift of Pentacene Thin-Film Transistors and Inverters with Al2O3 Gate Dielectric. *Appl. Phys. Lett.* 2007, 90, No. 133503.

(15) Dey, A.; Singh, A.; Kalita, A.; Das, D.; Iyer, P. K. High Performance, Low Operating Voltage n-Type Organic Field Effect Transistor Based on Inorganic-Organic Bilayer Dielectric System. *J. Phys.: Conf. Ser.* 2016, 704, No. 012017.

(16) Gou, H.; Wang, G.; Tong, Y.; Tang, Q.; Liu, Y. Electronic and Optoelectronic Properties of Zinc Phthalocyanine Single-Crystal Nanobelt Transistors. *Org. Electron.* 2016, 30, 158–164.

(17) Noh, Y. Y.; Kim, D. Y.; Yase, K. Highly Sensitive Thin-Film Organic Phototransistors: Effect of Wavelength of Light Source on Device Performance. *J. Appl. Phys.* 2005, 98, No. 074505.