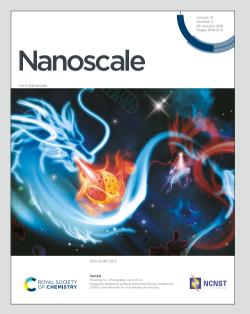
View Article Online View Journal

Nanoscale

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: V. D. Virole, N. B. Dabke, S. Verma, A. Kumar, R. Pandya, S. Husale, K. Vanka, R. G. Gonnade and R. Kanawade, *Nanoscale*, 2025, DOI: 10.1039/D4NR05252H.



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

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

You can find more information about Accepted Manuscripts in the Information for Authors.

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



rsc.li/nanoscale

ARTICLE

Received 00th January 20xx.

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x Investigating visible range photoresponse of organic single-crystal of green fluorescent protein analogue

Vishal Virole,^{a,b} Niteen Dabke,^{a,b} Sahil Verma,^{b,c} Ajay Kumar,^{a,b} Rinu Pandya,^{a,b} Sudhir Husale,^{b,c} Kumar Vanka,^{a,b} Rajesh Gonnade,^{a,b} and Rajesh Kanawade^{*a,b}

The growing demand for lightweight, flexible, semi-transparent and low-cost photodetectors (PDs) in wearable electronics and optical communication systems has promoted studies to investigate organic materials as feasible alternatives to conventional inorganic PDs. However, modern organic PDs often demonstrate responsivity, detectivity, and photoresponse speed limitations, particularly in the visible range. Here, we present the photoresponse of the organic single-crystal analogue of the Green Fluorescent Protein (GFP) chromophore photodetector, fabricated on a silicon nitride substrate. A significant increase in photocurrent was detected upon illumination with visible wavelengths (532 nm, 630 nm, and Halogen light). A remarkably consistent and repeatable photoresponse was obtained during the On and OFF illumination cycles. A device showed the dependence of photocurrent on the applied bias voltages. The measured photocurrent, responsivity, detectivity, rise times & decay times, noise equivalent power and external quantum efficiency are studied for different wavelengths. Strikingly, the fabricated device demonstrates excellent performance in the visible region compared to several conventional organic and inorganic PDs. The observed responsivity and detectivity values for the device are 98 mA/W and 7.94 x 10⁸ Jones respectively. Furthermore, the device also exhibits rapid photoresponse dynamics with a rise time of 180 ms and a decay time of 152 ms. The excellent photodetection features indicates that the single crystal GFP could serve as a versatile broadband material for future applications in optoelectronics.

1. Introduction

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32

Photodetectors (PDs) are the devices that convert optical signals into electrical outputs, are essential components across various applications, including imaging¹, medical diagnostics², distance measuring³, optical signal communications⁴, etc. Currently, inorganic materials such as silicon (Si), germanium (Ge), indium gallium arsenide (InGaAs), and compounds such as III-V semiconductors dominate the commercial PD market.⁵ These materials are wellknown for their high sensitivity, charge-carrier mobility, stability, and rapid response times.⁶⁻⁸ Furthermore, inorganic photodetectors (IPDs) exhibit excellent integration with existing electronics systems, ensuring their suitability for compact minuscule photodetectors and other specialized devices. However, the practical applications of commercial inorganic photodetectors is constrained by several drawbacks, including complex and expensive manufacturing processes and mechanical inflexibility, especially in terms of demand for large, flexible and affordable devices. They are inherently rigid and fragile, expensive, requires complex processing, and necessitate a low-temperature cooling system during operation.9

To overcome the challenges, organic photodetectors (OPDs) have

gained significant attention in the last 20 years due to their inherent advantages, such as low fabrication costs, light weight properties, material tunable properties, semi-transparency, solution processibility, and mechanical flexibility, which effectively offsets the limitations of conventional inorganic photodetectors.¹⁰⁻¹² They also possess superior photoelectrical properties due to their large absorption coefficient than that of inorganic materials. Organic materials, unlike their inorganic counterparts, are processable at low temperatures and their direct fabrication onto soft flexible substrates is easy. They also possess superior photoelectrical properties due to their large absorption coefficient.¹³⁻¹⁵ Due to their well ordered molecular packing, absence of any grain boundaries and reduced trap density, organic crystalline materials are being increasingly used in photodetection and wearable electronic devices.¹⁶ Photodetectors with a significant performance in ultraviolet-visible (UV-Vis) to near-infrared (NIR) region have immense potential in various applications, such as in medical diagnostics, imaging, night time monitoring, quality control check, and visual recognition system.¹⁷⁻²² Hence, organic materials because of their promising properties are attractive candidates for broadband flexible devices.

Furthermore, novel broadband OPDs with that are sensitive to UV,-Vis, and NIR wavelengths have been introduced as well. For example, PM6:BTP-eC9 OPD system operating in UV-Vis-NIR region is demonstrated using a cost-effective processing strategy with high performance.²³ Qi et al. demonstrated the application of PSeTPTI as a donor material in phototransistor (PT) OPDs with high-

^aPhysical & Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune, Maharashtra, 411008, India Email: <u>rv.kanawade@ncl.res.in</u>

^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India ^cQuantum Nanophotonics Metrology Division, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi, 110012, India

oscale Accepted Manus

Journal Name

View Article Online

ARTICLE

performance, and thermal stability. This material showed a wide absorption spectrum spanning from the UV to the visible range and could prolong the response time due to the presence of electron traps.²⁴ Also, in flexible devices, demonstration of CuPc/PC₆₀BM on flexible PET substrates and 10 mm² of active area highlights its improved responsivity in the visible spectrum.²⁵ Furthermore, organic single crystals of pentacene demonstrated remarkable performance in the visible region (532 nm and 658 nm).¹⁶ Despite their potential, only a few research efforts have focused on high-performance OPDs based on organic single crystals. As However, extensive efforts are being made to improve the electrical performance of OSCs.

Hence our aim in this study is to explore the organic crystalline materials with significant photoelectrical properties and flexibility and holds potential to be used in next generation wearable devices. Here, we report a single crystal analogue of the green fluorescent protein (GFP), for visible range photodetection. GFP exhibits strong light absorption properties, outstanding charge transport properties and is mechanically flexible. While other GFP chromophore analogues have shown promise in optoelectronic applications, most research has been centred around their photoluminescent functionalities, particularly in areas such as security tags, bioimaging and biosensing devices.²⁶⁻²⁸ In our previous study, we have explored this material for optical waveguiding capabilities and potential applications in fluorescent inks.²⁶ Despite its excellent optical properties, GFP single crystal-based photodetectors are not been reported yet. Furthermore, GFP analogues can be a promising candidate for photodetector applications due to their bandgap of around 2.8 eV, inherent ability to efficiently generate electron-hole pairs upon light absorption, and good charge separation properties. Hence, the effort of this study is to investigate GFP single crystal analogue for photoresponse measurements.

In this study, we evaluated the photocurrent response of the GFP single crystal under varying applied bias voltages and using three distinct light sources to thoroughly examine its performance across different illumination conditions. The resulting photodetector exhibits a remarkable photo response, with high responsivity and detectivity values when exposed to a 532 nm, 630 nm laser and Halogen light source, indicating its excellent potential for visiblerange photodetection applications. The device demonstrates excellent photodetection performance with fast response speeds (rise and decay times), comparable responsivity (R), detectivity (D), high external quantum efficiency (EQE) and improved noise equivalent power (NEP). A proportional investigation including the optical analysis using UV-visible (UV-Vis) and photoluminescence (PL) spectroscopy, High-resolution transmission electron microscopy (HR-TEM) and time dependent density functional theory calculations were performed. The results imply that the synthesized high-quality crystals shows great technological potential for the development of next generation efficient and sensitive photodetectors in the visible range.

2.1. Synthesis

A GFP chromophore analogue was prepared according to a previously reported method. The synthesis involved multiple steps, starting with the condensation of an aromatic aldehyde with a primary amine to form a Schiff base.^{26, 29} This Schiff base then reacted with an imidate intermediate in a (2+3) cycloaddition reaction, yielding the GFP chromophore analogue, **A**. Crystallizing compound A with Toluene resulted in the formation of plate-like crystals, designated as Form **A1**.

2.2. Material characterizations

Absorption spectra and photoluminescence of the Form A1 crystal were measured using UV- Vis spectrophotometer (model UV 3092, Labindia) and fluorescence spectrometer (Edinburgh Instruments, Model FS5 spectrofluorometer), respectively. High-resolution transmission electron microscopy (HRTEM) images obtained with JEOL JEM F-200 instrument, operating at 200 kV. The CSI Nano-Observer AFM instrument was utilized to measure the topography. Kelvin probe force microscopy (KPFM) was used to measure work function of the sample which works by measuring the contact potential difference (CPD) between a conductive AFM tip and the sample surface, analyzing long-range electrostatic forces generated by the probe-sample interactions³⁰. The Pt/Ir coated calibrated KPFM tip with work function (Φ) value of 4.85 eV was utilized for the surface potential measurements. Furthermore, the crystal was analysed using the Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations performed with the Gaussian 09 software package. The B97D3³¹ functional, incorporating Grimme's D3³² dispersion correction, was employed at 6-311G(d,p)³³ basis set level to evaluate the HOMO-LUMO gap and to gain insights into the UV-Vis absorption spectra.

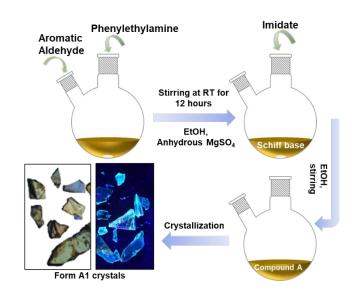


Fig. 1 Schematic diagram of the growth of a Form A1 single-crystal.

2. Materials and Methods

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32.

Journal Name

ARTICLE

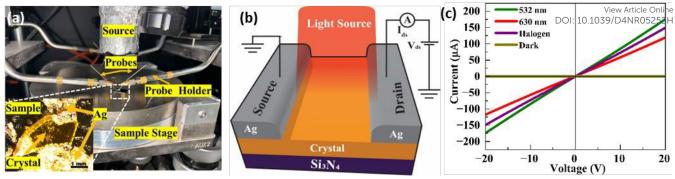


Fig. 2 (a) Experimental setup, MPS150 Cascade Microtech EPS150TRIAX probe station. Inset shows the optical image of crystal (b) Schematics of the photocurrent measurement. (c) Form A1 crystal I-V curves for 532 nm, 630 nm, Halogen and in dark.

2.3. Experimental setup for photocurrent analysis

The photodetector device was fabricated using a single-crystal of A1 GFP, which was carefully positioned on a silicon nitride substrate. The crystal was aligned on the substrate to achieve optimal contact and effective interaction with the incident light. Silver (Ag) paste was carefully applied to form source and drain contacts on the crystal to establish electrical connections. The silver paste was chosen for its excellent conductivity and ease of application, enabling low-resistance electrical pathways³⁴. The contacts were manually placed using a precision tip to ensure minimal damage to the crystal surface and uniform distribution of the paste, thereby enhancing charge injection and minimizing contact-related losses. The photocurrent measurements of the crystal was evaluated in a probe station (EPS150TRIAX, Cascade Microtech). A Keithley 2634B source meter was employed to measure the electrical response, including I-V curves and time dependent photocurrent. The device was illuminated with two available laser sources at 532 nm (486 mW/cm²) and 632 nm(78 mW/cm²) and a broadband Halogen lamp for photocurrent measurements. The effective illumination area of the crystal was approximately 36 μ m², and the light was directed onto the active region to ensure uniform exposure. The power density of all light sources was calibrated and maintained at a constant level throughout the experiments to ensure reproducibility and allow for direct comparison of the device performance under different illumination conditions. The time-dependent photocurrent measurements of the device was recorded at several applied bias voltages, ranging from ±2V, ±5V, ±7.5V, ±10V, ±15V, and ±20V. This was done to evaluate the device's responsivity under various operating conditions. The dynamic response of the photodetector was measured under ON/OFF light cycles after every five seconds interval of time to assess its stability, rise time, and decay time at each bias voltage.



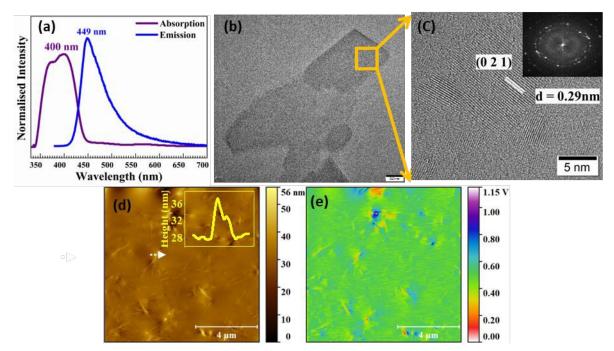
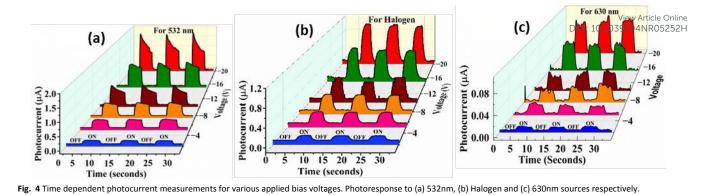


Fig. 3 (a) The Form A1 absorption and photoemission spectra, (b and c) HRTEM image of the crystal (inset shows SAED pattern), (d) AFM micrograph of the crystal; inset illustrates the height profile indicated by the white dashed line, (e) Surface potential map obtained by KPFM.

Nanoscale Accepted Manus



3.1. Characterization and measurements

Photoluminescence (PL) and absorption properties were studied for the optical characterisation studies. Fig. 3(a) shows the absorption and emission spectra of the crystal at ambient temperature within the wavelength range of 300-700 nm. The analysis revealed an absorption maximum at 400 nm and an emission peak at 449 nm, which corresponds to the crystal's characteristic blue emission. The optical bandgap of the material was calculated using the Tauc relation, yielding a value of 2.84 eV. This value closely matches the theoretical values predicted by DFT calculations. This consistency between experimental and computational results emphasizes the material's optical properties and applicability for visible-range photodetection applications.

HRTEM of Form **A1** crystal was performed. Fig. 3(b and c) revealed well-defined lattice fringes, indicating a high degree of crystallinity, essential for charge transport and optoelectronic applications³⁵. The lattice fringes observed in the HRTEM micrographs correspond to an interplanar spacing of approximately 0.29 nm which represents the (021) plane. The selected area electron diffraction (SAED) pattern represents the

single crystalline nature of the material.

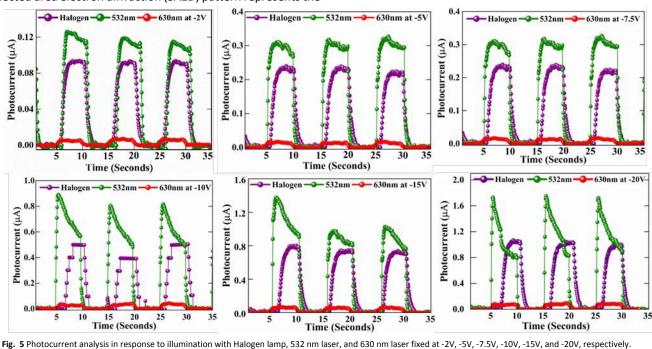
Atomic Force microscope (AFM) in tapping mode was employed over a 10 x 10 μm^2 area to characterize the surface morphology shown in Fig 3(d). The inset shows the height profile indicating the relatively smooth and uniform surface profile which is crucial for reliable photodetector performance.

To further characterize the electrical properties of the crystal, we performed KPFM measurements, an electrical mode of AFM, allows for the determination of work function, surface potential and charge distribution.³⁶ Fig. 3(e) portrays the surface mapping of the crystal over 10 x 10 μ m² area. The CPD between the tip and the sample is expressed as³⁷:

$$CPD = \frac{\phi_{tip} - \phi_{sample}}{-e},\tag{1}$$

Where Φ_{tip} and Φ_{sample} represents the work functions of the tip and sample, respectively. In Fig. 3e, CPD between tip and sample can be seen clearly. Thus, the material's work function evaluated as 5.25eV by using the equations 2 and 3.

$$(\phi_{sample} - \phi_{tip}) \approx 0.4 eV,$$
 (2)



Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32.

Journal Name

3.2. Time-dependent photocurrent analysis

Fig. 4 depicts the time-dependent photocurrent response of the Form A1 GFP single crystal photodetector under six different bias voltages and illuminated by three different light sources, with 'ON' indicates the light exposure. The photocurrent Iph was estimated using the relation $I_{ph} = I_{light}$ - $I_{dark}\text{,}$ where I_{light} and I_{dark} are the currents measured when the lights were turned ON and OFF, respectively. The photocurrent exhibited a clear dependence on the applied bias voltage, indicating enhanced separation and drift of photogenerated carriers, with the maximum photocurrent observed at -20V for all light sources. Specifically, the 532 nm laser at 486mW/cm² shows the highest response, with the photocurrent increasing from 0.008 µA at -2V to 1.73 µA at -20V. Also, a maximum photocurrent of 0.06 μ A for 630 nm at (78 mW/cm²) and 1.0 μ A for the Halogen lamp is observed. This indicates the material's optimal sensitivity is in the visible spectrum. The device also demonstrated excellent photocurrent stability across multiple ON/OFF cycles, showing consistent and repeatable behaviour under all light sources, emphasizing the material's robustness and reliability.

For comparative analysis of the photoresponse to different light sources, we plotted the time-dependent photocurrent curves for various voltages, as shown in Fig. 5. This highlights the photodetector's wavelength selective sensitivity and performance consistency under varying illumination sources and bias conditions. Furthermore, the device maintained excellent photocurrent stability across all light sources, with negligible fluctuation in current during repeated ON/OFF cycles, indicating reliable performance under various illumination sources.

 Table 1. Transient photocurrent response of Form A1 GFP single

 crystal

decay time, noise equivalent power and external quantum efficiency. DOI: 10.1039/D4NR05252H

Responsivity, refers to the ratio of output photocurrent to the power of incident light at a given wavelength, provides a direct measure of the device's efficiency in converting light into optical signals^{38, 39} In this study, the responsivity of the **A1** GFP photodetector was found to rise significantly upon applied bias voltage, reaching a maximum of 98.89 mA/W at -20V under 532 nm illumination. This enhanced responsivity at higher bias voltages can be attributed to the increased separation and mobility of photogenerated carriers, leading to stronger photocurrent.⁴⁰ This shows the superior performance of the device in the visible spectrum. This characteristic is crucial for imaging or optical communication applications, where precise light detection in specific wavelengths is needed.

Detectivity, expressed in cm Hz^{1/2} W⁻¹ or Jones, measures the photodetector's sensitivity to weak optical signals.⁴¹ It considers both the responsivity and noise in the system, which provides a more comprehensive measure of performance. Our photodetector exhibits a maximum detectivity of 7.94×10^8 Jones at 532 nm under -20 V bias, making it highly competitive with conventional organic photodetectors. The high detectivity is associated with low dark current and efficient charge transport within the **A1** GFP crystal structure.¹² This minimizes thermal noise and improves the signal-to-noise ratio, enabling the device to detect faint light signals precisely.

These responsivity and detectivity parameters can be calculated using equations 4 and 5.

$$R = \frac{I_{\rm ph}}{P_{\rm d} \times A},\tag{4}$$

$$D = \frac{R_{\rm ph}\sqrt{A}}{\sqrt{2eI_{\rm d}}},$$
 (5)

Laser Wavelength (nm)	Bias Voltage (V)	Responsivity (mA W ⁻¹)	Detectivity (Jones)	Rise time (ms)	Decay time (ms)	EQE (%)	NEP WHz ^{-1/2}
532	-2	6.94	2.09×10^{8}	279	217	1.62	2.30 × 10 ⁻¹¹
	-5	20.56	3.09×10^{8}	218	186	4.80	2.52 × 10 ⁻¹¹
	-7.5	30.91	4.09×10^{8}	232	238	7.21	2.53 × 10 ⁻¹¹
	-10	51.49	4.33×10^{8}	194	208	12.01	2.28 × 10 ⁻¹¹
	-15	78.32	6.83×10^{8}	159	191	18.27	2.29 × 10 ⁻¹¹
	-20	98.89	7.38×10^{8}	180	152	23.07	2.38 × 10 ⁻¹¹
630	-2	2.10	6.66×10^{7}	593	536	0.49	4.14 × 10 ⁻¹¹
	-5	7.04	1.41×10^{8}	553	431	1.64	3.58 × 10 ⁻¹¹
	-7.5	8.55	1.39×10^{8}	434	511	2.00	3.99 × 10 ⁻¹¹
	-10	11.18	1.57×10^{8}	547	484	2.61	4.04 × 10 ⁻¹¹
	-15	22.64	2.59×10^{8}	480	533	5.28	3.49 × 10 ⁻¹¹
	-20	27.95	2.75× 10 ⁸	547	585	6.52	3.65 × 10 ⁻¹¹

where, A is the active area, P_d is the power flux density, and e is the charge of an electron.

3.3. Performance parameters of a photodetector

The performance of a photodetector device was evaluated based on different figures of merit. To examine the device's photoresponse, it is essential to evaluate some of the important parameters which includes responsivity, detectivity, rise time, This indicates that the responsivity is a function of both the effective area and the laser power. Fig. 6 (a and b) shows the responsivity and detectivity response of the device at various applied voltages and in response to both laser wavelengths. Higher bias voltages resulted in increased responsivity for all

Journal Name

light sources. The Table 1 describes the photocurrent response of Form **A1** single crystals to various laser wavelengths and applied voltages. EQE and NEP, two additional performance parameters were also extracted using the following equations:

$$EQE = \frac{Rhc}{q\lambda} \times 100$$
 (6)

$$NEP = \sqrt{\frac{2qI_d}{R}}$$
(7)

Where h is the plank's constant and c is the speed of light.

The EQE, which measures the number of charge carriers generated per incident photon, demonstrates the superior performance of this GFP-based photodetector.⁴² At 532 nm, the EQE reaches 23.07% under -20 V bias, significantly improving the photodetection capabilities by effectively converting incoming photons into electrical signals. Despite a reduced bias of -2 V, the EQE remained stable at 1.62%, demonstrating the material's capacity to sustain good performance across diverse operating conditions. The enhanced EQE is crucial for applications which require efficient light-to-electrical energy conversion, including imaging systems and optical sensors. The NEP refers to the minimal optical power needed for the detector to generate a signal that is comparable to the noise level, hence defining the weakest light signal detectable by the device.⁴³

A lower NEP value reflects a more sensitive photodetector. This study reveals that the **A1** GFP photodetector exhibits an

Table 2 Summary of parameters used in this work.

532 nm (486 mW/cm ²)		
)		
36 μm²		
ilicon nitride		
400 nm		
449 nm		
(8)		
(9)		

Where $I_{0,} \tau_r$, τ_d , and A_0 represents the saturated photocurrent,

rise time constant, decay time constant and fitting parameter,

 $(a)_{100}$ (b) 532 nm (486 mWcm⁻²) 30 630 nm (78 mWcm-2) x 10⁸ - Responsivity · Responsivity 2 5 Responsivity (mA/W) Responsivity (mA/W) Detectivity Detectivity 25 80 **Detectivity (Jones)** 6 2.0 20 60 5 1.5 15 40 4 10 1.0 3 20 5 0.5 2 0 0 5 10 -15 -20-10 -15 -20 0 Voltage (V) Voltage (V) (c) 0.35 2.0 (d) Rist time fit -5V -Decay time fit 532 nm 630 nm 0.30 Halogen Photocurrent (mA) Photocurrent (µA) 0.25 Light OFF τ_d=269ms =218m 0.20 1.(0.15 532nm (486mW/cm² 0.10 0.5 0.05 ight ON 0.0 0.00 -20 ·10 15 15 Time (Seconds) 20 Voltage (V)

Fig. 6 (a) Responsivity and Detectivity of the device for 532 nm, (b) 630 nm (c) Decay and rise times of photocurrent, (d) Photocurrent vs Voltage response for 532 nm, 630 nm and Halogen.

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32.

Detectivity (Jones)

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32.

Journal Name

ARTICLE

View Article Online

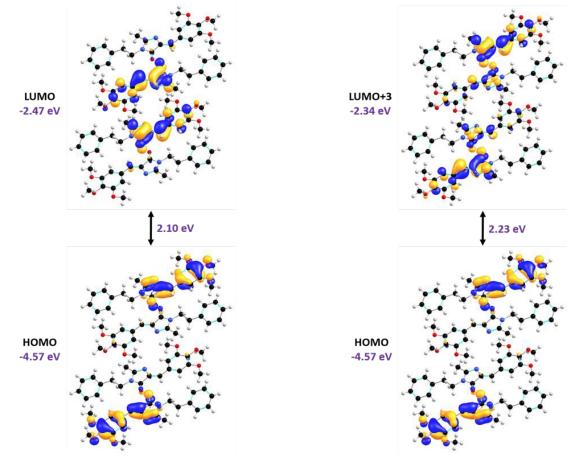
respectively. The fitting curve obtained from these equations gives the rise and decay time constants.

As shown in Fig. 6(d), the photocurrent vs. voltage plot highlights the stability and reproducibility of the **A1** GFP photodetector's performance. This indicates minimal fluctuations in photocurrent, demonstrating consistent response across multiple measurements. The photocurrent rises proportionally as voltage increases, reaching its maximum at -20V, reflecting optimal carrier separation and mobility. The device also shows reliable performance at lower voltages, making it suitable for low-power applications.

A comparative analysis of the performance metrics (responsivity and detectivity) of the **A1** GFP analogue and other reported materials is presented in Table 3. This comparison highlights the significant advancements achieved in this work. Notably, the **A1** GFP single crystal exhibits a comparative responsivity to conventional organic and inorganic photodetectors reported in recent literature. The table further shows that the rise and decay times of the **A1** GFP device are competitive, with values of 180 ms and 152 ms, respectively, demonstrating fast photoresponse dynamics compared to other materials. This comprehensive comparison positions the **A1** GFP analogue as a superior candidate for next-generation visible-range photodetectors, providing a balance between high sensitivity, fast response, and robust material stability.

3.4. Computational studies

Density functional theory (DFT) calculations were carried out on Form A1 crystal by B97D3/6-311G(d,p) level of theory. The HOMO to LUMO gap explains charge transport mechanism within the Form A1 crystal, where electron density is transferred from the conjugated imidazole moiety and the trimethoxybenzene moiety at the outer regions to the inner parts of the same moieties, as illustrated in Fig. 7. Timedependent density functional theory (TD-DFT) calculations at the B97D3 level were performed to compare the experimentally obtained bandgap of the Form A1 crystal. It was observed that the transition corresponding to the λ_{max} (f_{osc} = 0.5616, ^{calcd} λ_{abs} = 419.64 nm, $^{exp}\lambda_{abs}$ = 400 nm) is originating from a $\pi \rightarrow \pi^*$ transition between the HOMO and the LUMO+3 orbitals. During this transition, the HOMO is predominantly delocalized across the π molecular orbitals of the conjugated imidazole and trimethoxybenzene rings, and the LUMO gets delocalized across the π^* molecular orbitals of this same rings and the π^* orbitals of the C=C bonds. Additionally, the small HOMO-LUMO gap facilitates efficient photoexcitation, allowing the crystal to readily absorb photons and promote electrons from the HOMO to the LUMO. This characteristic improves the ability of the material to generate charge carriers upon light absorption, making it suitable for use in photodetector. The reduced energy barrier for electron excitation improves its sensitivity to light, enabling faster response times and efficient photocurrent



generation, which are essential properties for photodetection applications.

wearable devices, where its flexibility and lightweight nature allow seamless integration. DOI: 10.1039/D4NR05252H

Table 3 A table comparing the key characteristic parameters of the photodetectors investigated in this work with those of previously reported organic/inorganic photodetectors.

Material	λ	Bias	R	D	Ref
	(nm)	(V)	(mA/	(Jones)	
			W)		
$MoS_2/g-C_3N_4$	532	-9	700	8×10^{10}	44
ZnInS4 single	460	10	170	1.7×10^{12}	45
crystals					
Benzothiophene	405	-	420	-	46
PBTB	1122	8	0.96	-	47
Alq3	254	5	14.5	2.0×10^{12}	48
TESAN-BT	550	70	50	2 × 10 ⁹	49
Graphene/penta	480	-	7	2 × 10 ⁹	50
cene/ PTCDI-C8					
C60 single	400	10	8.0	7.08×10^{8}	51
crystal arrays					
Form A1 crystal	532	-20	98.89	7.94 x10 ⁸	This
	630	-20	27.95	2.75× 10 ⁸	Work

3.5. Discussion and future prospects

Form A1 crystal shows the better efficiency for generation of free charge carriers upon light absorption and charge transport under the influence of external potential. The delocalized nature of π -conjugated system in the molecule facilitates the efficient charge transport, allowing separated charges to migrate towards the electrodes which is crucial for photodetector performance. Although our device shows excellent photodetection performance in the visible spectrum, future studies should explore the photodetector's sensitivity across a broadband spectrum from UV and near-infrared (NIR) regions. The performance of the device has been studied under constant laser power settings; however, it can be explored for varying laser intensities which could provide deeper insights into its photodetection performance. It should be noted that, the experiments in this work were performed in the controlled environmental conditions i.e., at ~ 25 °C and humidity: 50-60%. Therefore, further studies with varied environmental conditions will be required for assessing the device's performance, stability, and robustness for its practical deployment, particularly in wearable or outdoor devices. Further, other analogues of this family can be synthesised and studied for highperformance broadband photodetectors with good stability and mechanical flexibility.

In medical diagnostics, it can be used in non-invasive monitoring devices like smartwatches or skin sensors to track vital signs using light-based methods. Its biocompatibility and high sensitivity make it ideal for implantable biosensors and optical communication systems, ensuring real-time data transmission and environmental sensing. Further, the GFPbased photodetector holds significant promise for practical applications in flexible electronics, such as foldable displays and

4. Conclusions

In this study, we successfully demonstrate the potential of a Green Fluorescent Protein (GFP) chromophore analogue as an organic single-crystal photodetector, particularly for visible-range applications. The synthesized **A1** GFP crystals exhibit significant values of device parameters, including responsivity & detectivity. The peak photocurrent of 1.73 μ A was achieved under a bias voltage of -20V. The photodetector's rapid response times, with a rise time and decay time, further highlight its suitability for fast photodetection applications. These features make the **A1** GFP analogue highly adaptable for next-generation technologies.

Author contributions

V. V.: conceptualization, writing– original draft and formal analysis; N.D.: Methodology; S.V.: resources, validation; A.K.: editing, validation; R.P.: resources; S.H.: Methodology, resources, and review & editing; R.G.: Resources; K.V.: resources; R.K.: supervision, project administration, methodology, conceptualization and review & editing.

Data Availability

The data supporting the findings of this work are available within the article.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledges the Director of CSIR-NCL, Pune, India, for the opportunity and infrastructure to conduct this research, and to the Director of CSIR-NPL, Delhi, India, for providing the experimental facility and guidance. The V.V. acknowledge DST, and INSPIRE (DST/INSPIRE/03/2023/000261) for the research fellowship. The financial support from the Science and Engineering Research Board (SERB), New Delhi (Grant No. CRG/ 2022/004504) is acknowledged by RGG and RVK. K.V. aknowledges DST-SERB (CRG/2021/003255) for financial support. For computational facilities, R.P. and K.V. acknowledges Multi-Scale Simulation and Modeling project (MSM). The "PARAM Brahma Facility" under National Supercomputing Mission, Government of India, (IISER, Pune) is acknowledged.

References

 Y.-L. Wu, K. Fukuda, T. Yokota and T. Someya, *Adv. Mater.*, 2019, 31, 1903687.

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32.

8 | J. Name., 2012, 00, 1-3

Published on 27 februari 2025. Downloaded on 10/03/2025 21:43:32

Journal Name

- 2. C. M. Lochner, Y. Khan, A. Pierre and A. C. Arias, *Nat. Commun.*, 2014, **5**, 5745.
- Y. Wang, J. Benduhn, L. Baisinger, C. Lungenschmied, K. Leo and D. Spoltore, ACS Appl. Mater. Interfaces, 2021, 13, 23239-23246.
- M. Babics, H. Bristow, W. Zhang, A. Wadsworth, M. Neophytou, N. Gasparini and I. McCulloch, *J. Mater. Chem. C*, 2021, 9, 2375-2380.
- 5. B. Biswas and B. Saha, *Phys. Rev. Mater.*, 2019, **3**, 020301.
- M. Shahbaz, M. A. Butt and R. Piramidowicz, *Micromachines*, 2023, 14, 1637.
- 7. J. E. Carey and E. Mazur, San Francisco, California, 2004.
- W. Si, W. Zhou, X. Liu, K. Wang, Y. Liao, F. Yan and X. Ji, Micromachines, 2024, 15, 427.
- 9. Q. Li, Y. Guo and Y. Liu, Chem. Mater., 2019, 31, 6359-6379.
- C. Fuentes-Hernandez, W.-F. Chou, T. M. Khan, L. Diniz, J. Lukens, F. A. Larrain, V. A. Rodriguez-Toro and B. Kippelen, *Science*, 2020, **370**, 698-701.
- 11. Y. Xu and Q. Lin, Appl. Phys. Rev., 2020, 7.
- 12. D. Yang and D. Ma, Adv. Opt. Mater., 2019, 7, 1800522.
- 13. W. Wu, K. Chen, T. Wang, N. Wang, X. Huang, L. Zhou, Z. Wang and H. Hao, *J. Mater. Chem. C*, 2023, **11**, 2026-2052.
- S. Qin, X. Qin, Q. Du, Y. Gan, Y. Zhang, A. Wang, X. Yan, R. Dong, Y. Liu, S. Li, C. Liu, W. Wang and F. Wang, *J. Mater. Chem. C*, 2022, **10**, 11710-11718.
- 15. M. Wang, Y. Xiao, Y. Li, L. Han, Z. Sun, L. He, R. Liu and K. Hu, *Materials*, 2022, **15**, 4820.
- Q. Du, Z. Wang Du, M. Li Du, Y. Gan, S. Li, Y. Liu, W. Wang, F. Wang and S. Qin, J. Mater. Chem. C, 2023, 11, 5182-5189.
- H. Lee, E. Kim, Y. Lee, H. Kim, J. Lee, M. Kim, H.-J. Yoo and S. Yoo, Sci. Adv., 2018, 4, eaas9530.
- N. Li, N. Eedugurala, D.-S. Leem, J. D. Azoulay and T. N. Ng, *Adv. Funct. Mater.*, 2021, **31**, 2100565.
- 19. H.-R. Lim, H. S. Kim, R. Qazi, Y.-T. Kwon, J.-W. Jeong and W.-H. Yeo, *Adv. Mater.*, 2020, **32**, 1901924.
- D. Tordera, B. Peeters, H. B. Akkerman, A. J. J. M. van Breemen, J. Maas, S. Shanmugam, A. J. Kronemeijer and G. H. Gelinck, *Adv. Mater. Tech.*, 2019, 4, 1900651.
- G. Simone, M. J. Dyson, S. C. J. Meskers, R. A. J. Janssen and G. H. Gelinck, *Adv. Funct. Mater.*, 2020, **30**, 1904205.
- Z. He, J. Han, X. Du, L. Cao, J. Wang, C. Zheng, H. Lin and S. Tao, Adv. Funct. Mater., 2021, **31**, 2103988.
- H. Thachoth Chandran, H. Tang, T. Liu, S. Mahadevan, K. Liu, Z. Lu, J. Huang, Z. Ren, F. Liao, Y. Chai, P. W. Fong, S.-W. Tsang, S. Lu and G. Li, *Mater. Horiz.*, 2023, **10**, 918-927.
- Z. Qi, J. Cao, H. Li, L. Ding and J. Wang, *Adv. Funct. Mater.*, 2015, 25, 3138-3146.
- 25. B. Nath, P. C. Ramamurthy, D. R. Mahapatra and G. Hegde, 2022.
- N. B. Dabke, Y. Raut, B. P. Mali, R. Pandya, K. Vanka, K. Manoj and R. G. Gonnade, *J. Mater. Chem. C*, 2024, **12**, 8368-8379.
- 27. D. H. Lambert GG, Gotthard G, Schultz DT, Navizet I, Lambert T, et al., *PLoS Biol.*, 2020, **18**.
- 28. F. Tian, G. Xu, S. Zhou, S. Chen and D. He, *Analyst*, 2023, **148**, 2882-2891.
- 29. A. Baldridge, J. Kowalik and L. M. Tolbert, *Synthesis*, 2010, **2010**, 2424-2436.
- S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132.
- A. D. McLean and G. S. Chandler, *The J. Chem. Phys.*, 1980, **72**, 5639-5648.

- Y. Hwang, Y. H. Hwang, K. W. Choi, S. Lee, S. Kim_{v/Sw}J_ArPack and B.-K. Ju, *Sci. Rep.*, 2021, 11, 10499.
 DOI: 10.1039/D4NR05252H
- 34. T. Xiao, J. Wang, S. Yang, Y. Zhu, D. Li, Z. Wang, S. Feng, L. Bu, X. Zhan and G. Lu, *J. Mater. Chem. A*, 2020, **8**, 401-411.
- M. Nonnenmacher, M. P. O'Boyle and H. K. Wickramasinghe, Appl. Phys. Lett., 1991, 58, 2921-2923.
- 36. S. Sorifi, S. Kaushik and R. Singh, *Nanoscale Adv.*, 2022, **4**, 479-490.
- R. Shikler, T. Meoded, N. Fried, B. Mishori and Y. Rosenwaks, J. Appl. Phys., 1999, 86, 107-113.
- W. Feng, J.-B. Wu, X. Li, W. Zheng, X. Zhou, K. Xiao, W. Cao, B. Yang, J.-C. Idrobo, L. Basile, W. Tian, P. Tan and P. Hu, *J. Mater. Chem. C*, 2015, **3**, 7022-7028.
- L. Lv, J. Yu, X. Sui, J. Wu, X. Dong, G. Lu, X. Liu, A. Peng and H. Huang, J. Mater. Chem. C, 2019, 7, 5739-5747.
- 40. K. Roy, M. Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan and A. Ghosh, *Nat. Nanotechnol.*, 2013, **8**, 826-830.
- 41. S. Verma, R. Yadav, A. Pandey, M. Kaur and S. Husale, *Sci. Rep.*, 2023, **13**, 197.
- X. Liu, D. Wang, P. Shao, H. Sun, S. Fang, Y. Kang, K. Liang, H. Jia, Y. Luo, J. Xue, J. Wang, T. Zhi, D. Chen, B. Liu, S. Long and R. Zhang, *Adv. Funct. Mater.*, 2022, **32**, 2201604.
- I. K. Kim, J. H. Jo, J. Lee and Y. J. Choi, Org. Electron., 2018, 57, 89-92.
- D. B. Velusamy, M. A. Haque, M. R. Parida, F. Zhang, T. Wu, O. F. Mohammed and H. N. Alshareef, *Adv. Funct. Mater.*, 2017, 27, 1605554.
- L. Valdman, V. Mazánek, P. Marvan, M. Serra, R. Arenal and Z. Sofer, Adv. Opt. Mater., 2021, 9, 2100845.
- Y. Zhou, L. Wang, J. Wang, J. Pei and Y. Cao, *Adv. Mater.*, 2008, 20, 3745-3749.
- L. Lv, W. Dang, X. Wu, H. Chen, T. Wang, L. Qin, Z. Wei, K. Zhang, G. Shen and H. Huang, *Macromol.*, 2020, 53, 10636-10643.
- Y. Zhang, J. Jie, Y. Sun, S. G. Jeon, X. Zhang, G. Dai, C. J. Lee and X. Zhang, *Small*, 2017, 13, 1604261.
- D. S. Chung, Y.-H. Kim and J.-S. Lee, Nanotechnology, 2014, 25, 035202.
- J. S. Kim, Y. J. Choi, H. J. Woo, J. Yang, Y. J. Song, M. S. Kang and J. H. Cho, *Adv. Funct. Mater.*, 2017, 27, 1704475.
- S. Zheng, X. Xiong, Z. Zheng, T. Xu, L. Zhang, T. Zhai and X. Lu, Carbon, 2018, **126**, 299-304.

This journal is © The Royal Society of Chemistry 20xx

Nanoscale Accepted Manuscript

Data Availability

The data supporting the findings of this work are available within the article.