



Water-based fluorescent flexo-ink for security applications

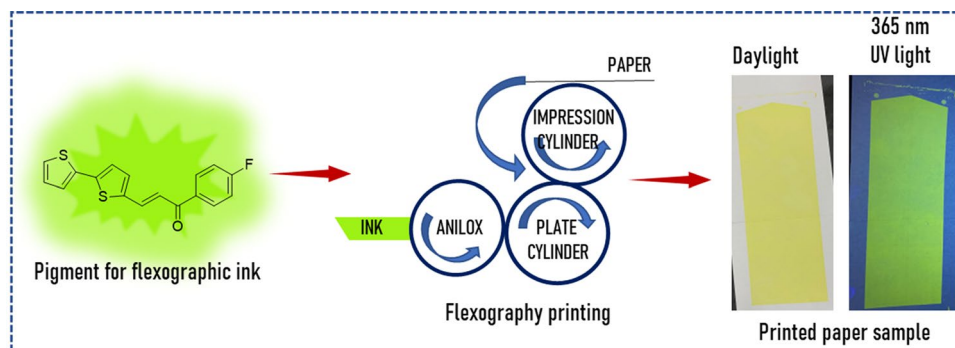
Kashmitha Muthamma¹ · Basana M. Gouda¹ · Dhanya Sunil¹ · Suresh D. Kulkarni² · Anand P.J.³

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Abstract

UV-readable fluorescent ink formulations find versatile applications in various fields including information encryption, automated identification systems, security markers and optical devices. In this context, a new bithiophene-based chalcone (BTCF) that exhibits good solution phase and solid-state fluorescence was synthesized as a colourant for formulating an eco-friendly UV fluorescent ink. The molecule demonstrated good thermal stability and photophysical features including intramolecular charge transfer, confirmed through emission studies in THF–hexane mixtures with varying hexane content. The intense greenish yellow solid-state fluorescence emission displayed by BTCF was exploited by using it as a colourant in a water-based fluorescent ink formulation. Further, the ink was used to print a fast-drying solid patch on an UV dull paper substrate using flexography technique. The analysis of colorimetric, densitometric and rub resistance properties of the printed paper samples demonstrated good fluorescence, moderate photostability and good rub resistance, and hence could be used for security printing applications.

Graphical abstract



Keywords Bithiophene · Chalcone · Water-based formulation · UV fluorescent flexo-ink · Security printing

Introduction

Fluorescent inks have extensive applications in wide areas including security printing, smart packaging products, certificates, information storage, bioimaging, highlighting markers, fluorescent tags, nanoelectronics, etc. (Liu et al. 2019). Moreover, there is a high demand for water-based fluorescent ink formulations, which is a greener approach wherein the water replaces the organic solvents (Muthamma et al. 2020). They are more environment-friendly as they emit less volatile organic compounds, thereby lesser pollution and better safety as the main benefits. In addition, these inks being less

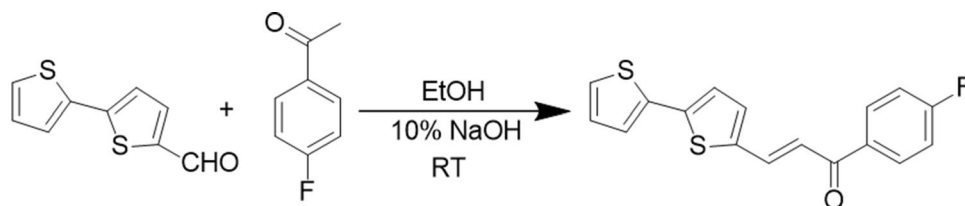
✉ Dhanya Sunil
dhanyadss3@gmail.com

¹ Department of Chemistry, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

² Department of Atomic and Molecular Physics, Centre for Applied Nanosciences, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

³ Manipal Technologies Limited, Manipal, Karnataka 576104, India

Scheme 1 Synthetic route of BTCF



flammable aids in easier storage when compared to solvent-based inks. These eco-friendly fluorescent inks are popular for flexography printing, as they can be easily dried on highly absorbent substrates with excellent permeability, and can also withstand high temperature (Ramirez and Tumolva 2018; Jingxiang et al. 2019; Zołek-Tryznowska and Izdebska 2013; Zołek-Tryznowska et al. 2015). Security printing using fluorescent inks can be adopted to realize various types of anticounterfeit technologies such as water marking, barcode, smart packaging and information encryption (Abdelhameed et al. 2021). Therefore, the use of luminescent pigments with good optical properties suitable for security printing have gained wide research interest.

The pigments used in fluorescent security inks should satisfy few stringent requirements including small particle size suitable to all printing processes, excellent resistance to commonly used solvents, chemicals, acids, soaps and detergents, along with good optical properties, lightfastness and rub resistance. Lanthanide-doped molecules (Yao et al. 2019), carbon dots (Qu et al. 2012; Kalytchuk et al. 2018), plasmonic materials (Tian et al. 2016; Duempelmann et al. 2017) and conventional organic materials have been investigated as pigments in security ink formulations in the recent past. Conventional organic molecules that own different carbon frameworks and/or carry other heteroatoms (N, O, S, etc.) including coumarin (Ataefard and Nourmohammadian 2015; Talebnia et al. 2020), fluoran (Yang et al. 2019), benzothiazole (Echeverri et al. 2020), imidazole (Nadamani et al. 2019), tetraphenylethylene (Peng et al. 2019), naphthalene (Chen et al. 2019b), anthracene (Prusti and Chakravarty 2019) and pyrene (Wakchaure et al. 2019) have been investigated as pigments in solvent-based fluorescent inks. However, only few organic molecules such as coumarin (Ataefard and Nourmohammadian 2015), fluorene (Muthamma et al. 2021) and pyrene (Chen et al. 2019a; Bhagya et al. 2021) have been explored as colourants in water-based security inks.

Bithiophene is a naturally occurring environmentally stable heterocycle with two coplanar rings, each incorporating a sulphur atom. Formerly, the use of this moiety in optical applications was limited due to low fluorescence quantum yields in both solid and solution state. The efficient inter-system crossing of heavy sulphur atom, well-organized solid-state packing, relaxation of excited state through interannular rotations within the molecular framework and

aggregation-induced quenching might have contributed to the low emission quantum yield of thiophene-based materials (Rasmussen et al. 2015). Regardless of this limitation, various tactics have been developed to fabricate highly fluorescent thiophene-based materials over the last few years. Recent advances in constructing highly fluorescent materials by smartly tuning the inherent bithiophene-based structural framework offer ample impetus to construct newer derivatives for emissive applications. These sulphur containing small molecules are of substantial interest for versatile applications in organic electronics, as fluorescent biomarkers, sensors, security agents, etc. due to the possibility of controlled tuning of absorption and emission colour and good charge mobility (Perepichka and Perepichka 2009). Nevertheless, this molecular framework has not been investigated till date as a colourant in water-based flexo-ink formulations.

Chalcones are widely used for various applications due to their excellent fluorescent properties (Komarova et al. 2015), mainly due to the push–pull conjugation effect. Moreover, these materials have good thermal stability which is essential for long life time when used in various applications such as for printing or in electronic devices (Karuppusamy et al. 2017). Hence, the present study focuses on the synthesis as well as structural, optical, and thermal characterization of BTCF, a 2,2'-bithiophene incorporated chalcone with delocalized π -electrons and push–pull conjugation. Further, BTCF was used as a fluorescent pigment to formulate a water-based, eco-friendly ink for flexography printing. The fast-drying prints which displayed good optical and rub resistance features could be used for wide range of applications.

Results and discussion

Structural characterization of BTCF

The base catalysed aldol condensation between 2,2'-bithiophene-5-carboxaldehyde and 4-fluoroacetophenone generated the chalcone 3-([2,2'-bithiophen]-5-yl)-1-(4-fluorophenyl)prop-2-en-1-one (BTCF). Scheme 1 depicts the synthetic pathway for the chalcone.

The chemical structure of BTCF was established using spectral techniques as given below. The IR spectrum established the presence of enone linkage in the molecule (Fig.

S1). The NMR spectra: ^1H (Fig. S2a), ^{19}F (Fig. S3) and ^{13}C (Fig. S4) were in conformity with the chemical structure of the new chalcone. The Fig. S2b depicts the ^1H NMR spectrum of the solvent used. All the eleven protons in BTCF resonated between 6.9 and 8.0 ppm. The carbonyl carbon resonated at 187.95 ppm in the ^{13}C spectra, whereas the ^{19}F spectra provided the evidence of fluorine in the structural framework of BTCF. The mass spectrum (Fig. S5) was in agreement with the molecular mass of the bithiophene derived chalcone.

3-([2,2'-bithiophen]-4-yl)-1-(4-fluorophenyl)prop-2-en-1-one (BTCF): golden yellow (84.75%) m.p: 116–118 °C; FTIR (cm^{-1}): 1645 (C=O *str.*), 1562 (C=C *str.*), 1018 (C–F *str.*); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 6.985–7.006 (t, 1H), 7.089–7.132 (m, 3H), 7.167–7.241 (m, 4H), 7.816–7.854 (d, 1H), 7.965–7.999 (dd, 2H); ^{19}F NMR (376 MHz, CDCl_3 , ppm): δ –105.69; ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 115.65, 115.87, 119.73, 124.64, 124.97, 125.91, 128.19, 130.92, 131.01, 133.69, 134.52, 136.68, 137.24, 138.85, 140.93, 166.88, 187.95; Mass spectra $\text{C}_{17}\text{H}_{11}\text{FOS}_2$ (m/z): 315.0155.

Optical features and thermal stability of BTCF

The absorption and emission spectral traces of the chalcone were analysed to comprehend the optical properties. As presented in Fig. S6, the solution of BTCF in THF (1×10^{-5} M) showed two distinguished absorption bands at ~ 273 nm and ~ 398 nm due to the electronic transitions of the conjugated structural framework (Wang et al. 2017a, b; Zhang et al. 2017; Yang et al. 2020). The intense solid-state emission of BTCF is observed at 550 nm as shown in Fig. 1a, and the respective chromaticity diagram (Fig. 1b) indicates greenish yellow-coloured fluorescence. The emission spectra of BTCF solution in THF (1×10^{-5} M) depicted in Fig. 1c exhibits two prominent peaks at around ~ 408 nm and 432 nm when excited at 370 nm. Further, the emission features of BTCF in 1×10^{-5} M THF/THF–hexane mixtures were examined to check the effect of polarity of solvents on the fluorescence emission. The spectral variations of BTCF perceived in pure THF and upon increasing percentage volume of non-polar hexane is shown in Fig. 1d. The emission was blue-shifted from 432 to 425 nm with decrease in intensity, indicating the presence of an intramolecular charge transfer (ICT) process in the molecule (Sowmiya et al. 2011).

Thermal stability of pigments can be determined by thermogravimetric analysis (TGA), and the thermogram of BTCF as shown in Fig. S7 displayed a two-step weight loss. The chalcone is stable up to 250 °C as evident from the TGA plot and an initial 87% weight loss is detected from ~ 253 to 361 °C, which might be due to the partial decomposition of the compound (Naik et al. 2020).

Assessment of fluorescence property of the printed paper samples

As fluorescent materials have been widely used for various applications, especially security printing, BTCF was used as a pigment to formulate a fluorescent ink, which showed bright greenish yellow fluorescence when exposed to 365 nm UV light (Fig. S8a). The ink formulation, which was prepared as discussed in the experimental section comprised of BTCF pigment that served as the colouring and fluorescing component in the ink, whereas the vehicle of the ink consisted mainly of water as solvent along with other additives (Muthamma et al. 2021). The ink formulation with particle size of ~ 5 μm was used to print a patch on UV dull paper substrate using flexography. The printed paper samples dried quickly at room temperature and exhibited a greenish yellow fluorescence emission under 365 nm UV light source as portrayed in Fig. S8b. Further the excitation and the emission spectra of the printed sample (BP1) as shown in Fig. 2a were analysed. Upon excitation at 475 nm, the prints emitted at 540 nm. A slight blue-shift in the emission of the prints compared to the solid-state emission of BTCF (550 nm) could be due to the presence of ink components. The ink was further manually coated onto the UV dull paper using a zero numbered bar coater and the photographs of the coated paper (BC1) in daylight and under 365 nm UV light is presented in Fig. S8c. The intensity of emission from the coated paper (BC1) is found to be more than that of the print (BP1) as evident from Fig. 2b because of a thicker ink layer deposited during the coating process. Furthermore, the photostability of the prints were investigated by passing the printed paper sample under 300 W UV light for 0 (BP-0), 10 (BP-10), 20 (BP-20), 30 (BP-30), 40 (BP-40) and 50 (BP-50) passes, wherein the samples are exposed to UV light for 3–4 s during each cycle. The emission spectra of these samples are shown in Fig. 2c and it is perceived that fluorescence intensity of the UV exposed samples decreased with increase in exposure cycles.

Colorimetric analysis of the printed paper samples

The colorimetric measurements are easy and simple and can be used to determine the colour coordinates. In general, the $L^* a^* b^*$ international standard colour space specifies the numerical colour values as it is closer to the human perception of colour. The colour space and the values are utilized to develop and visualize colour in 2D or 3D spaces (Subhashree et al. 2017). The colour transformations of the printed samples were investigated and analysed using CIELAB colour space measurements. The $L^* a^* b^*$ colour coordinates of the flexo-printed paper samples for different cycles of UV exposure are listed in Supplementary Table S1, and the respective colorimetric plots are depicted in Fig. 3a.

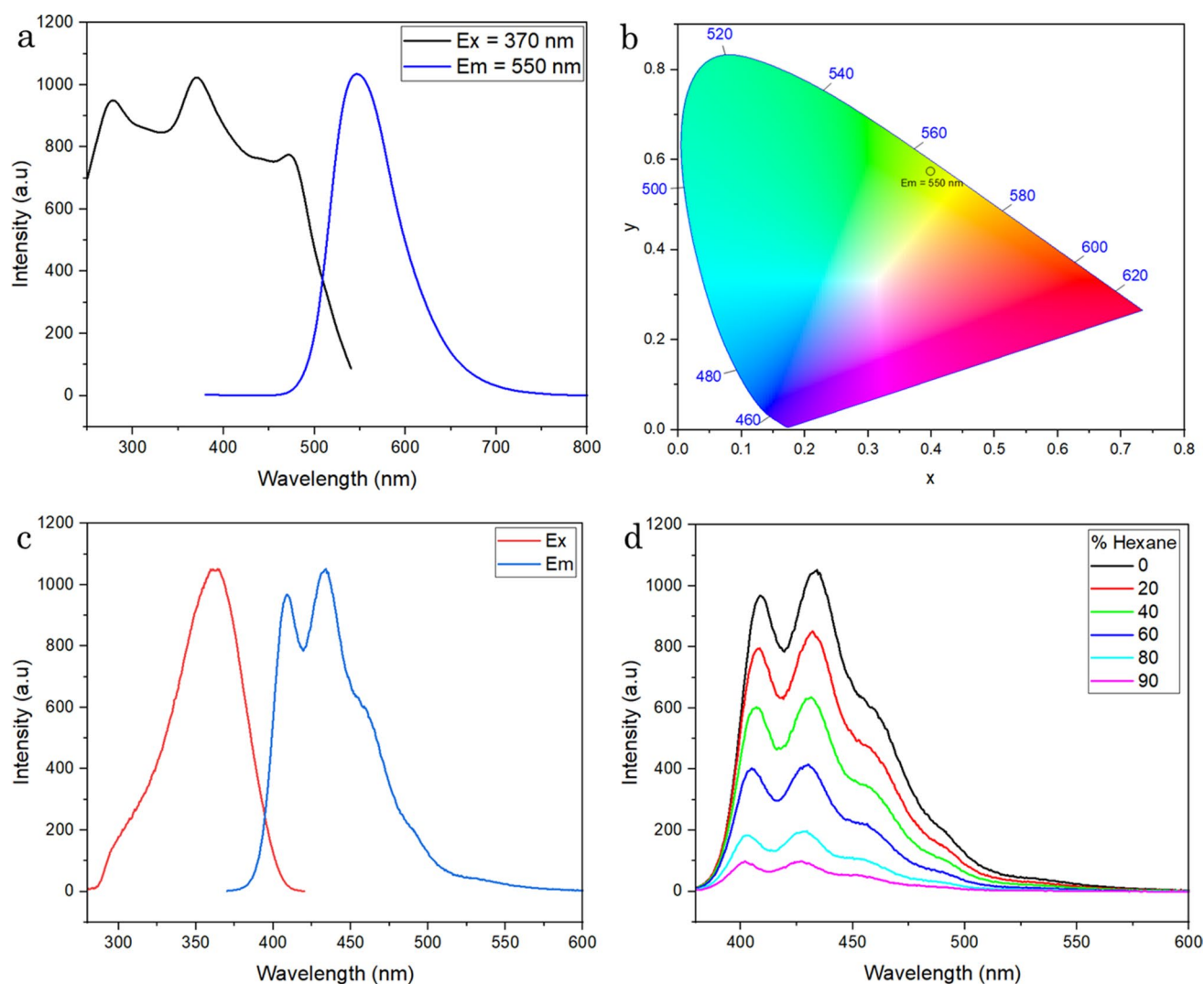


Fig. 1 BTCF in solid state; $\lambda_{\text{ex}}=370$ nm **a** excitation and emission spectra and **b** CIE plot. BTCF solution (1×10^{-5} M); $\lambda_{\text{ex}}=370$ nm: **c** excitation and emission spectra in THF and **d** emission spectra of BTCF in THF/THF–hexane mixtures

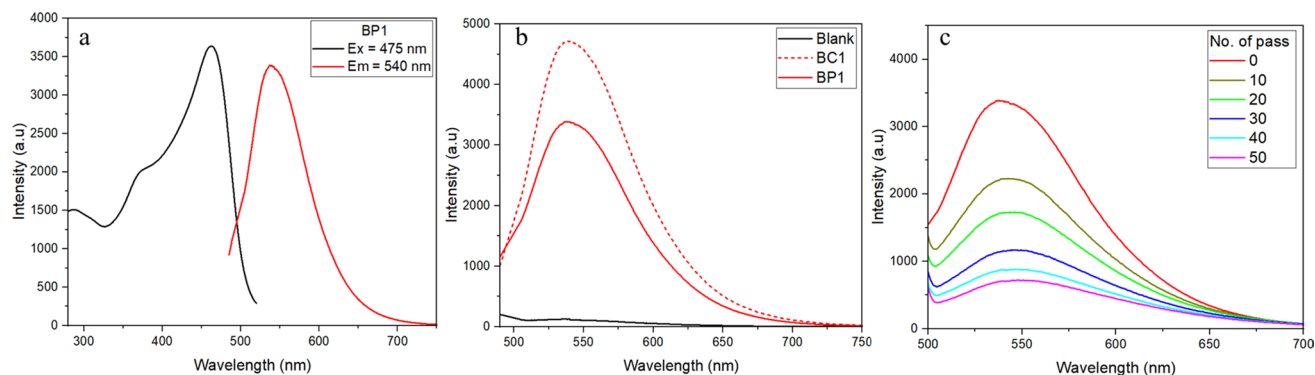


Fig. 2 **a** Excitation and emission spectra of the printed paper sample (BP1); $\lambda_{\text{ex}}=475$ nm, **b** emission spectra of the unprinted (blank), printed (BP1) and coated (BC1) paper samples, and **c** emission spec-

tra of printed paper samples after different cycles of exposure to 300 W UV light (30 m/min)

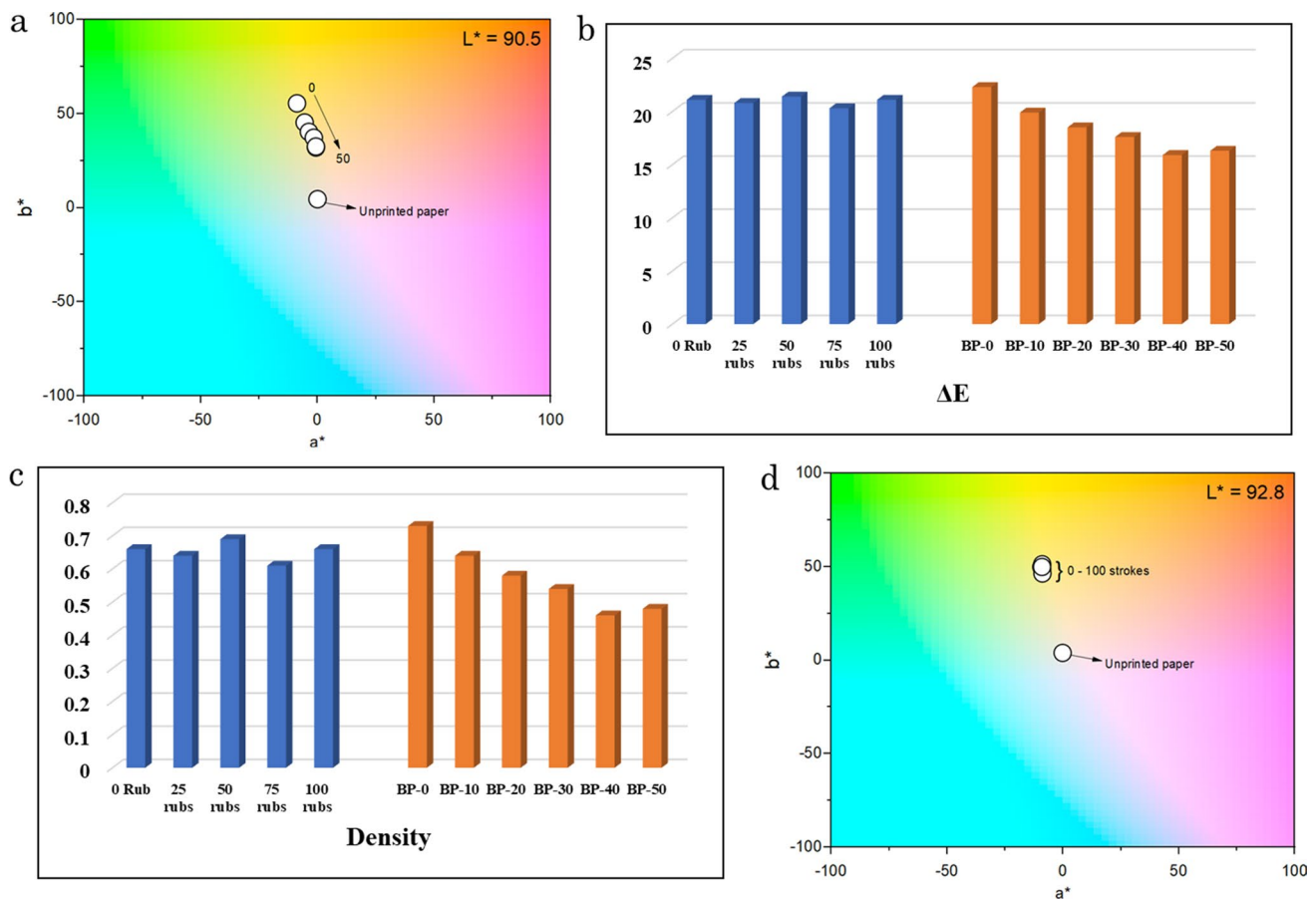


Fig. 3 CIE $L^* a^* b^*$ -2D scatter plots for printed paper samples before and after **a** different exposure cycles under UV 300 W/30 m/min and **d** after rub test. Plots of **b** ΔE and **c** density values from colorimetric studies

The unprinted paper sample was slightly off-white with 94.5 (L^*), -0.2 (a^*), 3.9 (b^*), 0.6 (ΔE) and 0.1 (density) as the colorimetric values. Upon increasing the number of UV exposure cycles, the $L^* a^* b^*$ values were found to slightly deviate from the unprinted sample with a shade alteration from greenish yellow to pale yellow as observed from Fig. 3. The ΔE and densitometric plots are depicted in Fig. 3b and 3c.

The rub resistance of the print is yet another important parameter that determines the degree of repeated rubbing or scuffing the print can withstand. The rub test was performed to stimulate the amount of damage on repeated rubbing and to assess the ability of the print to resist it. The rub test as described in the experimental section was performed, where the printed samples were tested for 25, 50, 75 and 100 rubs, and after each set of rubs, the colorimetric values were recorded. The values obtained are presented in Table S1 and pictorially depicted in Fig. 3d, which indicate that there is negligible change in the colour parameters between the rubbed and the zero-rubbed samples. Moreover, the good rub resistance feature of the print is also evident from the

ΔE and density values, which did not alter significantly as displayed in the plots (Fig. 3b and 3c).

Surface morphological topographies of the print

SEM and AFM techniques were used to examine the surface topographical features of the unprinted and printed samples, and the resulting microscopic images are presented in Fig. 4. The unprinted substrate exhibited a fibrous surface texture in the SEM images (Fig. 4a), whereas the printed paper sample posed a smoother surface (Fig. 4b) because the flexo-print creates a uniform and consistent ink film on the porous and fibrous paper substrate. Furthermore, from the AFM images displayed in Fig. 4c and d, the maximum roughness value (R_{max}) for the printed paper sample was 146 nm when compared to 346 nm of the unprinted paper sample (Table S2). It is evident that the ink film has decreased the surface roughness of the paper.

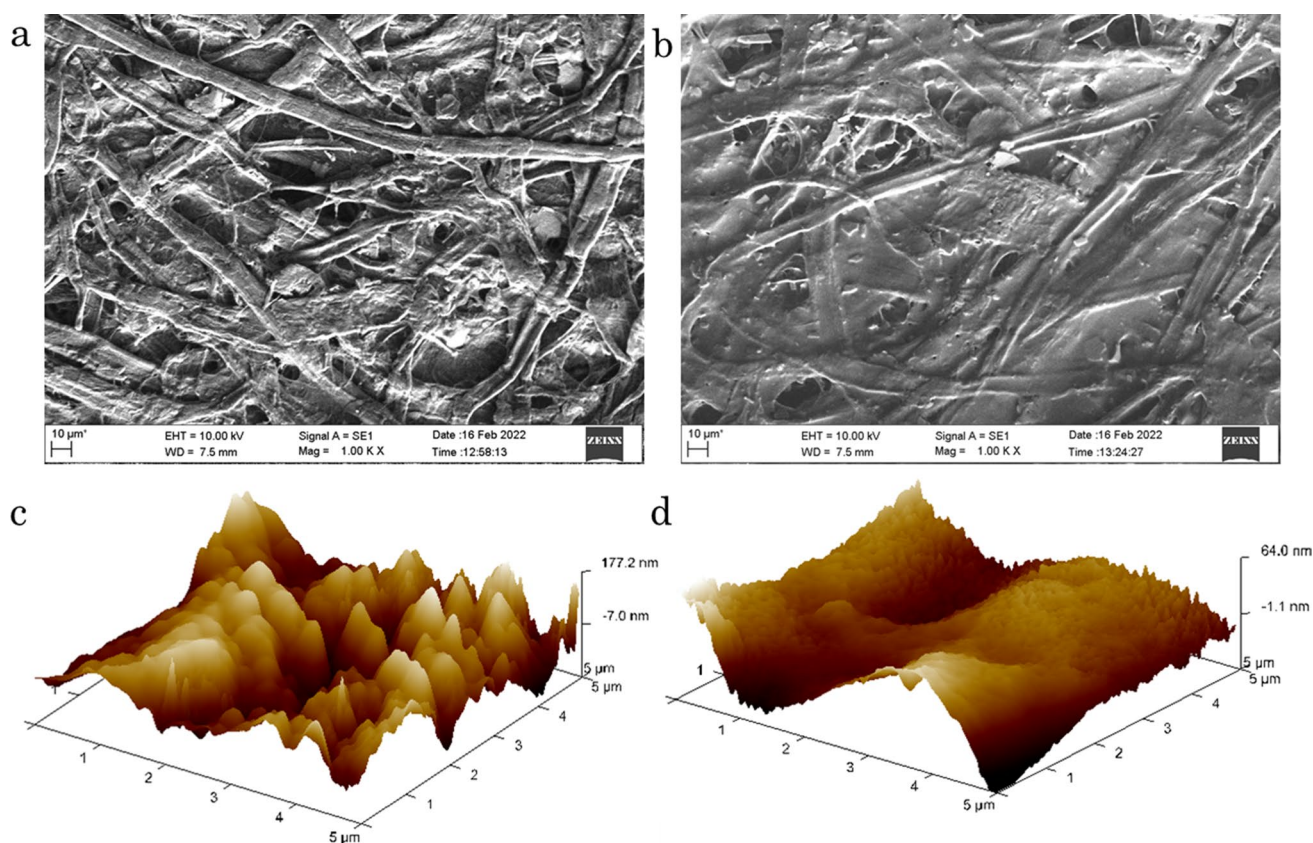


Fig. 4 SEM images of **a** unprinted and **b** flexo-ink printed paper sample. AFM images of **c** unprinted and **d** flexo-ink printed paper sample

Conclusion

In summary, we have synthesized a bithiophene-based chalcone (BTCF) for its plausible use as a pigment in UV-readable fluorescent ink formulation, which can extend real-life applications. The chemical structure of the colourant was established using spectral techniques. The fluorescent chalcone displayed several appealing properties including ICT and good thermal stability, and therefore served as a viable functional colourant for formulating a water-based eco-friendly ink. Flexography technique was used to effectively print the environment-friendly ink onto the porous paper surfaces. The prints demonstrated good adhesion and fast-drying on the porous substrate, moderate photostability, good abrasion resistance and fluorescence indicating its potential application in various fields including information encryption, data security, automatic identification, anticounterfeiting and optical devices (Nair et al. 2019).

Experimental

The chemicals and solvents used for the synthesis of BTCF were procured from Sigma-Aldrich and Spectrochem Chemicals Pvt. Ltd.

Synthesis of 3-([2,2'-bithiophen]-5-yl)-1-(4-fluorophenyl)prop-2-en-1-one (BTCF)

About 10% NaOH solution (0.5 mL) was added dropwise to a mixture of 4-fluoroacetophenone (1 mmol) and 2,2'-bithiophene-5-carboxaldehyde (1 mmol) in ethanol and stirred at room temperature (RT) for 5 h. The precipitate of BTCF formed was filtered, washed with water and dried.

The melting point of BTCF was determined using open capillary method. The FTIR and NMR spectra were recorded in ATR Shimadzu-IR Spirit analyser and 400 MHz Bruker spectrometer using CDCl_3 as solvent, respectively. The Xevo QToF MS system (Waters, USA) was used to record

the mass spectrum (HR-LCMS) of BTCF. The absorption and emission studies were performed using 1800 Shimadzu UV–visible spectrophotometer and JASCO spectrofluorometer FP 8300, respectively. The TGA was performed under nitrogen atmosphere at 10 °C min⁻¹ as the heating rate using HITACHI Simultaneous Thermogravimetric Analyzer STA7000 series.

The components used for preparing the ink formulation including acrylic emulsions, solvents and additives were obtained from Kamson's Pvt. Ltd, DOW Chemical Company, BASF—Chemicals and Evonik Industries. A mixture (wt%) of BTCF (12.36), acrylic emulsion 1 (66.24), wetting and dispersing agent (1.80) and diethylene glycol monoethyl ether (carbitol-19.60) were milled in the Llyod's pigment muller 92 N at 40 Kgf to obtain the ink concentrate. The remaining components were dispersed in the ink concentrate to obtain the final ink composition (wt%): pigment BTCF (7.70), acrylic emulsion 1 (52.50), acrylic emulsion 2 (15.05), wax (1.70), de-foamer (1.25), wetting and dispersing agent (1.15), carbitol (12.20), butyl carbitol (2.00), water (4.90) and 25% ammonia solution (1.55). Zehnter grindometer was used to measure the particle size of the ink.

The UV dull paper was used as substrate for printing, which was obtained from Manipal Press, Pvt Ltd, Manipal, India. The flexography printing was carried out using a RK Flexiproof 100 apparatus at a speed of 75 m/min with 9.5 BCM anilox roll, photopolymer plate and a chambered doctor blade inking system. The photostability of the ink was studied using a Hari Impex LAB UV 83002 instrument by exposing the prints under UV light of 300 W and belt rotation speed of 30 m/min. The rub test was carried out using a Sutherland ink rub tester by placing the printed paper against an unprinted paper on the test rubber pad with 4 lbs for 100 rubs. The colorimetric data were recorded using Xrite Ii Pro spectrophotometer. The CIE 3D colour coordinates explored includes L^* (indicates lightness; a value of 0 and 100 represent black and white, respectively), a^* (green for negative and red for positive a^* values) and b^* (blue for negative and yellow for positive b^* values), where the a^* and b^* values can range from -120 to 120. ΔE gives the colour differences and is calculated using the equation below (Zolek-Tryznowska and Izdebska 2013; Muthamma et al. 2021).

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where $(\Delta L^*) = L^*_{(u)} - L^*$, $(\Delta a^*) = a^*_{(u)} - a^*$ and $(\Delta b^*) = b^*_{(u)} - b^*$ are the differences between the printed paper samples and (u) is the unprinted sample/blank paper sample (Zolek-Tryznowska et al. 2015).

The surface morphologies of the printed and unprinted paper samples were recorded using Carl Zeiss EVO 18

analytical scanning electron microscope (SEM) and INNOVA SPM atomic force microscope (AFM).

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11696-023-02765-9>.

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Data availability The data are available upon reasonable request from the first author (KM).

Declarations

Conflict of interest The authors declare no conflict of interest with this work.

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