# Light-Induced Fabrication of Nanoporous Conductive PEDOT-PCL Scaffold: A Versatile Approach Combining Step-Growth and Chain-Growth Polymerizations

Tugberk Tabak<sup>1</sup>, Kerem Kaya<sup>1, \*</sup>, Recep Isci<sup>1</sup>, Turan Ozturk<sup>1,2,\*</sup>, Baris Kiskan<sup>1\*</sup>, and Yusuf Yagci<sup>1, †</sup>

<sup>1</sup> Istanbul Technical University, Chemistry Department, Maslak, 34469 Istanbul, Turkey

<sup>2</sup> TUBITAK UME, Chemistry Group Laboratories, Gebze, Kocaeli 54, 41470, Turkey

Corresponding e-mail addresses: <u>kkaya@itu.edu.tr</u>, <u>ozturktur@itu.edu.tr</u>, <u>kiskanb@itu.edu.tr</u>

+: This paper is dedicated to the memory of Prof. Yusuf Yagci.

**Abstract:** The field of developing electroconductive artificial scaffolds that can imitate the architecture of human tissues is growing rapidly. Poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(*ɛ*-caprolactone) (PCL) are the two gold standards for achieving the required conductivity and robustness in such materials. In this study, we present a novel light-induced method for fabricating a PEDOT-PCL scaffold using phenacyl bromide (PAB) as a single-component photoinitiator. The release of HBr from the step-growth polymerization of EDOT was utilized as *in situ* catalyst for the chain-growth polymerization of caprolactone. Detailed investigations revealed the formation of a self-assembled nanoporous electroconductive (1.2 mS/cm) scaffold which was characterized by several spectroscopic and microscopic techniques. The fluorescence emission spectra exhibited a mixed solvatochromic behavior, indicating specific interactions between the self-assembled scaffold, as evidenced by TEM, and solvents with varying polarities. Moreover, the same light-induced technique was applied for bulk photopolymerization showcasing the versatility and wide-ranging scope.

#### Introduction

Since their discovery in 1977, conducting polymers (CPs) have become highly appealing materials for a wide range of uses. These applications span across diverse fields including sensors<sup>1</sup>, capacitators<sup>2</sup>, solar cells<sup>3</sup>, drug delivery<sup>4</sup>, and wound dressing<sup>5</sup>. Especially, biocompatible CPs such as polyaniline (PANI)<sup>6</sup>, polypyrrole<sup>7</sup>, polythiophene<sup>8</sup>, and poly (3,4-ethylenedioxythiophene) (PEDOT)<sup>9, 10</sup> displayed promising features for biomedical utilizations. This is primarily due to their optical transparency, chemical stability, and cytocompatibility.

Among the stated CPs, particularly, PEDOT based materials have gained considerable attention in recent the decade due to their remarkable resistance to oxidation, low intrinsic cytotoxicity, and good mechanical strength<sup>11</sup>. These distinctive features have positioned PEDOTs as an attractive candidate for the fabrication of biodegradable and electroconductive polymers, particularly in the field of tissue engineering (TE) scaffolds<sup>12-17</sup>. In general, TE scaffolds are designed to be nanoporous, electroconductive, and biodegradable structures that can provide temporary support for tissue regeneration<sup>18-21</sup>. However, a critical challenge lies in the fact that PEDOTs, along with many other CPs, exhibits low or non-biodegradability, brittleness, and insolubility<sup>22, 23</sup>. These factors limit the standalone use of PEDOTs or other CPs as TE scaffolds.

Extensive efforts have been made to address the limitations encountered in the fabrication of tissue engineering (TE) scaffolds. Accordingly, PEDOT has been incorporated into biodegradable polymer matrices having high mechanical strength, biodegradability, and

good solubility in various solvents<sup>24</sup>. For example, several polymers, including polylactide (PLA)<sup>25</sup>, poly (methylmethacrylate) (PMMA)<sup>26</sup>, poly (vinyl alcohol) (PVA)<sup>27</sup> and poly  $\varepsilon$ -caprolactone (PCL)<sup>28-30</sup> have been utilized for this purpose. Among them, in particular, PCL has emerged as a prominent synthetic polymer for TE scaffolds due to its hydrophobicity, excellent thermoelasticity, and its ability to form polymeric blends<sup>31-34</sup>. Moreover, the long degradation time of PCL under physiological conditions, resulting from the hydrolytic chain scission of the ester groups, aligns well with the timeframe required for tissue regeneration or healing (typically 2-3 weeks)<sup>35</sup>. Another advantage of PCL is related to the ease of its synthesis, which involves ring-opening polymerization (ROP) of  $\varepsilon$ -caprolactone (ECL). Predominantly, pseudo-anionic pathway utilizing stannous octanoate (Sn(Oct)<sub>2</sub>)<sup>36-39</sup> are preferred in these syntheses. However, cationic pathways are also performed using cationic initiators. <sup>40</sup>

Accordingly, in recent years, various synthetic approaches have been explored for PEDOT-PCL scaffolds. For example, chemical oxidative (co)polymerization of monomers (EDOT and ECL) using FeCl<sub>3</sub> and stannous octanoate (Sn(Oct)<sub>2</sub>) in multiple-step reactions. <sup>41, 42</sup> In addition, electrooxidative polymerization of macromonomers, such as PCL-substituted EDOT, utilizing potentiostats<sup>43</sup>, and physical blending of PEDOT/PCL by (electro)spinning<sup>44</sup> or by vapor-phase polymerizations (VPP) are employed <sup>45</sup>. Although these methods are effective to some extent in the fabrication of scaffolds, they generally involve the use of corrosive chemicals and/or require high energy input or sophisticated experimental setups.

Considering the drawbacks associated with these existing methods, light-induced polymerization reactions are prominent alternative methods due to their high efficiency, low energy requirements, and mild conditions <sup>46-49</sup>. Furhermore, light-mediated polymerizations are particularly well-suited for 3D printing applications, including scaffold fabrication, owing to their unique capability for spatiotemporal control. In this way, the precise printing of scaffolds with desired shapes, sizes, and thicknesses is relatively simple and quick<sup>50</sup>. Fabrication of PEDOT-PCL scaffolds with a light-induced polymerization method can be considered as a favorable approach to eliminate some of the drawbacks of the previous methods. However, to the best of our knowledge, the synthesis of PEDOT-PCL (or any CP-PCL) scaffold with light-induced polymerizations has not been reported. Therefore, in this work, we report for the first time, lightmediated in situ fabrication of a PEDOT-PCL scaffold, using a single-component photoinitiator, namely, phenacyl bromide (PAB). The utilized system is based on the photoinduced stepgrowth polymerization of EDOT and harnessing the released HBr as an in situ catalyst for the ROP of ECL. The experimental results revealed the successful formation of a self-assembled nanoporous PEDOT-PCL scaffold with exceptional electroconductivity<sup>28, 51</sup>. Furthermore, bulk photopolymerization under visible light irradiation (415 nm) was succeeded which demonstrates the versatility of the proposed approach.

#### **Materials and Methods**

#### Materials

3,4-ethylenedioxythiophene (EDOT) (Sigma-Aldrich, 97%), diphenyliodonium bromide (DPIBr) (Sigma-Aldrich, %98), deuterated chloroform (CDCl<sub>3</sub>) (Merck, 99.8%) and deuterated dimethylsulfoxide (DMSO-d6) (Merck, 99.8%) were used without any purification. All the other

solvents used in this work were distilled according to conventional techniques before use. 2bromoacetophenone (PAB) (Sigma-Aldrich, 98%) was recrystallized from its hot ethanol solution and  $\varepsilon$ -caprolactone (Sigma-Aldrich, 97%) was vacuum-distilled over CaH<sub>2</sub> under nitrogen atmosphere prior to use.

#### Methods

#### Fabrication of PEDOT-PCL scaffold by photopolymerization

For UV-A initiated polymerization reaction, 500  $\mu$ L of EDOT (*ca.* 5 mmol), 500  $\mu$ L of ECL (*ca.* 5 mmol), 100 mg of PAB (*ca.* 5 mmol) were dissolved using 500  $\mu$ L dichloromethane (DCM) solvent inside a Schlenk tube which was previously heated-vacuumed-degassed three times using nitrogen gas. Schlenk tube was then placed inside a photo-reactor equipped with a magnetic stirrer, cooling fan and 18 fluorescent lamps (Philips TL 18W BLB) emitting light nominally at 355 nm with a light intensity of ~100 mW/cm<sup>2</sup> (measured using Delta OHM Quantum radio photometer) at reaction flask (Fig. S1). After 4 h of irradiation, the initial yellow colored reaction mixture turned to dark blue-black color (Fig. S2). Then, the mixture was precipitated into 10-fold methanol and the resultant dark blue/black colored solid was washed with n-hexane to remove the unreacted monomers, side product (acetophenone) and the catalyst. For visible light initiated bulk polymerization, 300 mg of PAB was dissolved in 1 mL mixture of EDOT and ECL (500  $\mu$ L of each) and was transferred into a Teflon mold which was later irradiated for 2 h using a Rofin Polilight PL400 equipped with a 400 W of metal halide lamp operating at 415 nm (Fig. S3).

#### Light-induced synthesis of homopolymers of PEDOT and PCL

For the synthesis of PCL, 720 mg (2 mmol) and 200  $\mu$ L of ECL (*ca.* 2 mmol) were dissolved using 500  $\mu$ L dichloromethane (DCM) solvent inside a Schlenk tube which was previously heated-vacuumed-degassed three times using nitrogen gas. Schlenk tube was then irradiated using a photo-reactor equipped with 3 fluorescent lamp (Crawl Miracle UVB 13W) emitting light nominally at 300 nm with a light intensity ~80 mW/cm<sup>2</sup> (measured using Delta OHM Quantum radio photometer) at reaction flask. After 4 h of irradiation, the solution was precipitated into 10-fold methanol and the resultant white colored solid was dried under vacuum. For the synthesis of PEDOT, 500  $\mu$ L of EDOT (*ca.* 5 mmol) and 100 mg of PAB (*ca.* 5 mmol) were dissolved using 500  $\mu$ L dichloromethane (DCM) solvent inside a Schlenk tube which was previously heated-vacuumed-degassed three times using nitrogen gas. Schlenk tube would be was irradiated inside the photo-reactor used for the scaffold synthesis. The dark-blue colored solution was precipitated into cold methanol and dried under vacuum.

**IR Measurements.** Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector. 32 scans were averaged.

**GPC Measurements.** Gel permeation chromatography measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature-controlled pump, a column oven, a refractive index (RI) detector, a purge and degasser unit and TSKgel superhZ2000, 4. 6mm ID x 15 cm x 2cm column. Tetrahydrofuran was used as an

eluent at flow rate of 1.0 mL.min<sup>-1</sup> at 40 °C. Refractive index detector was calibrated with polystyrene standards having narrow molecular-weight distributions. GPC data were analyzed using Eco-SEC Analysis software.

**NMR Measurements.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> and DMSO-d6 with tetramethylsilane as an internal standard) at 500 MHz and 125 MHz, respectively on an Agilent VNMRS 500 spectrometer at 25°C.

**SEM Measurements.** SEM measurements were performed using Zeiss Ultra Plus Field Emission Scanning Electron Microscope with EHT= 5.00 kV and probe at 200 nA.

**Conductivity Measurements.** Conductivity measurements were performed in air at room temperature using a HP3478A digital voltmeter, with a direct 4-wire resistance capability.

**TEM Measurements.** For TEM measurements, samples were deposited as 10  $\mu$ L of 1 mM of samples in ethanol solution on a copper support grid. TEM analysis was performed using a JEOL JEM-ARM200CFEG UHR microscope with a spherical aberration-corrected probe and equipped with a Gatan UltraScan camera model 994 US1000X.

Water Contact Angle Measurements. The water contact angles (WCAs) were measured using the sessile drop method with a water drop volume of 10  $\mu$ L on a contact angle system (Dataphysics, Contact Angle System OCA 20) at ambient temperature.

**UV and Fluorescence Measurements.** UV–visible spectra were recorded with a Shimadzu UV-1601 double-beam spectrometer equipped with a 50W halogen lamp and a deuterium lamp which can operate between 190nm-1100nm. All fluorescence spectra were recorded using Perkin-Elmer LS55 spectrometer performing between 200-800 nm wavelengths with 10 nm slit width.

**Electrochemical Measurements**. The electrochemical measurements were carried out by using CH Instruments 617D potentiostat–galvanostat system. The electrochemical cell containing a Ag wire as a reference electrode (RE), a Pt wire as counter electrode (CE) and glassy carbon as a working electrode (WE) immersed in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte under argon atmosphere. In addition, oxidation potential onsets determined from the cyclic voltammetry (CV) were used for the HOMO level calculations by using the equation  $E_{HOMO} = -e (E_{ox} - E_{Fc}) + (-4.8 \text{ eV})$  according to the ferrocene oxidation  $E_{(Fc/Fc^+)} = 0.41 \text{ V}$  as internal standard.

**PXRD Measurements.** Crystallographic identifications were accomplished by X-ray diffraction (XRD) method on a benchtop Rigaku Miniflex diffractometer with a Cu-K $\alpha$  radiation source operated at 30 kV and 10 mA. The acquisition angle ranged from 10° to 90°.

**DSC Mesurements.** DSC measurements were performed on a Perkin Elmer Diamond DSC 4000 with a heating rate of 10 K·min<sup>-1</sup> under nitrogen flow of 20 mL·min<sup>-1</sup>.

**TGA/DTA Measurements.** TGA/DTA measurements were carried out with a PerkinElmer Diamond TA/TGA instrument, USA at a heating rate of 10 °C/min from 25 to 800 °C under a nitrogen atmosphere (flow rate 40 mL·min<sup>-1</sup>).

#### **Results and Discussion**

The light induced synthesis of PEDOT using a single-component photoinitiator such as PAB, and the reaction mechanism of this polymerization was thoroughly studied by our group, previously.<sup>52</sup> PAB is known to undergo photodecomposition under UV-A light, generating phenacyl and bromine radicals<sup>53</sup>. The bromine radical then abstracts an electron from the highly electron-donating thiophene ring of EDOT to form an EDOT radical cation (EDOT<sup>++</sup>). The coupling between two EDOT<sup>++</sup> leads to the release of HBr, which can concomitantly act as an initiator for the cationic ROP of ECL<sup>54</sup>.

Thus, in the light of the previous studies, EDOT-ECL mixture was successfully photopolymerized in one-pot by using PAB to yield PEDOT-PCL scaffold. Besides, we proceeded with separate photopolymerization reactions of EDOT and ECL using PAB and DPIBr, respectively. This allowed us to compare the experimental results of the PEDOT-PCL scaffold with those of pristine PEDOT and PCL. The trials revealed that in the absence of EDOT in the reaction mixture, PAB does not initiate the polymerization of ECL due to the lack of HBr release. To simulate the light-induced release of HBr, we utilized DPIBr, which is known to generate HBr through the H<sup>+</sup> abstraction of bromide ions from the solvent or the other components under 300 nm irradiation. <sup>55</sup> The summarized pathways for all the light-induced polymerization reactions are presented in Scheme 1, along with images of the resulting polymeric products.



**Scheme 1.** Summarized reaction pathways for the light-induced polymerizations and images of the resulting polymers.

We first employed FTIR spectroscopy (Fig. 1) to conduct the analysis of the functional groups, present in the homopolymers and the scaffold (PEDOT-PCL). FTIR spectra of both model PCL and PEDOT are in accordance well with the literature<sup>56, 57</sup>. Similarly, FTIR spectrum of PEDOT-PCL exhibits transmittance at 3400 cm<sup>-1</sup> and 2850-2950 cm<sup>-1</sup> region, originating

from the hydroxyl group and aliphatic C-H stretching peaks belonging to PCL, respectively. Weak aromatic C-H stretching peaks around 3100 cm<sup>-1</sup> are attributed to the thiophene ring. Moreover, a shifting of the peaks towards average positions can be observed in the scaffold's spectrum compared with model PCL's and PEDOT's spectra. Notably, a significant change is observed in the fingerprint region and below 1750 cm<sup>-1</sup>, where the PEDOT-PCL spectrum exhibits two distinct carbonyl stretching peaks (vC=O) at 1721 cm<sup>-1</sup> and 1702 cm<sup>-1</sup>. While the peak at higher wavenumber is in accordance with PCL's spectrum, peak at lower wavenumber which doesn't belong to the carbonyl peak of the photoinitiator (PAB) or that of EDOT or ECL (Fig. S4). This could be attributed to the random attachment of the growing chains of PCL to PEDOT oligomers yielding a PEDOT-*ran*-PCL. Another support for the random attachment of thiophene rings was observed in the IR spectrum of the polymer sample taken after the first hour, where widely distributed multiple carbonyls in the lower wavenumbers were present (Fig. S5).



**Fig. 1** (a) IR spectra of PEDOT, PCL, PEDOT-PCL scaffold and its dedoped analogue (b) spectra focused on 2000-1000 cm<sup>-1</sup> region.

In addition, we investigated the molecular weights of the homopolymers and scaffold using gel-permeation chromatography (GPC). Reaction details, molecular weights, and polydispersity data of PCL, PEDOT and PEDOT-PCL scaffold are depicted in Table 1.

Monomer	Photoinitiator	Irradiation Wavelength (nm)	Conversion (%) <sup>b</sup>	<i>M</i> n (kDa) ⁰	а	Polymer
ECL	DPIBr	300	55	4.4	1.39	PCL
EDOT	PAB	355	82	32.5	1.35	PEDOT
EDOT + ECL	PAB	355	77	11.6	1.25	PEDOT-PCL
EDOT + ECL	PAB	415	38	8.95	1.27	PEDOT-PCL

Table 1. Light-induced polymerization results of ECL, EDOT, and EDOT-ECL mixture.<sup>a</sup>

[a] All the reactions were performed using 500  $\mu$ L DCM solvent except the visible light experiment (415 nm) which was performed in the absence of solvent (bulk system). More details of the photopolymerization procedures can be found in the methods section [b] Conversions were determined gravimetrically after the purification and drying of the samples. [c] Determined by GPC using a refractive index detector optimized with polystyrene standards and using a light-scattering detector.

GPC results of PCL exhibited polymeric species having broad molecular weight distribution due to the chain-growth nature of the polymerization reaction. GPC traces of PEDOT, on the other hand, revealed the formation of much larger molecular weight species with a dispersity of D = 1.35, which is close to the previous step-growth polymerization results of other electron-donor monomers such as *N*-ethylcarbazole<sup>58</sup>, *N*-methylpyrrole, and *N*-methylindole<sup>46</sup>. GPC traces of the PEDOT-PCL scaffold indicated the presence of polymers having average-molecular weight  $M_n$  closer to PCL's with slightly lower dispersity. From these data, it is possible to comment that the introduction of ECL interfered with the formation of high  $M_n$  PEDOT species. Bulk photopolymerization's conversion is relatively low, possibly due to the high viscosity resulting in low mobility and due to low penetration of the light at 415 nm. The lower  $M_n$  obtained in the bulk system can be attributed to the diminished efficiency of the PAB photoinitiator under visible light irradiation, as this was previously observed in the photopolymerization of EDOT.

<sup>1</sup>H NMR (Fig. 2a-b) and <sup>13</sup>C NMR (Fig. S6) spectra of the scaffold confirmed the presence of both polymers (PCL and PEDOT) inside the scaffold. All the peaks corresponding to PCL are in accordance with the literature<sup>59</sup>. The additional peak at 4.12 ppm belongs to the methylene group (-CH<sub>2</sub>) of ethylenedioxy moiety of PEDOT units. The absence of any significant aromatic peaks manifests the successful polymerization of EDOT. Photochemically synthesized pristine PEDOT was not soluble in CDCl<sub>3</sub>, however, the spectrum taken in DMSO-d6 solvent, contained one broad peak centered at 4.45 ppm (Fig. S7). Neglecting the solubility problems of PEDOT in chloroform, using the integrals from <sup>1</sup>H NMR, ~30% of PEDOT content is estimated in the scaffold.



**Fig. 2** (a) <sup>1</sup>H NMR spectrum of PEDOT-PCL scaffold measured in CDCl<sub>3</sub> (500 MHz) and (b) 0- 4.5 ppm region of the spectrum.

Following structural characterization by standard spectroscopic and chromatographic methods (IR, NMR, and GPC), surface morphology and topology of the homopolymers and scaffold were explored using scanning electron microscopy (SEM) (Fig. 3) and transmission electron microscopy (TEM) (Fig. 4), respectively.



Fig. 3 SEM micrographs of (a) PCL (b) PEDOT and (c) PEDOT-PCL scaffold.

Fig. 3 shows SEM micrographs of PCL, PEDOT, and PEDOT-PCL scaffold. Visual inspection of the images revealed that PCL displayed flake-like aggregates of crystals, while pristine PEDOT displayed a bulky amorphous morphology due to the stacking of the thiophene rings, restricting its use in many applications. On the other hand, the micrograph of the scaffold exhibited drastic differences and disclosed a spongy and interconnected nanoporous micelles morphology with pore sizes varying between 100-900 nm. An interconnected network is a desired feature for the possible cell migration within the scaffold<sup>60</sup>. Additionally, during SEM measurements, the PEDOT-PCL scaffold didn't require any Pt/Au coating which could be attributed to its electroconductivity which is later discussed. Based on SEM images, we can conclude that the incorporation of PCL into PEDOT, avoided the agglomeration of the aromatic units, resulting in a peculiar surface that resembles to the surface of the previously fabricated thiophene-containing PCL scaffolds. Furthermore, using energy dispersive x-ray spectroscopy (EDS) (Fig. S8), we calculated a ~25-30% PEDOT content (by comparing S to C ratio), which was close to the content calculated using NMR integrals.

Fig. 4 shows TEM micrographs of dilute ethanol dispersions of all the polymers with a 100 nm magnification. PCL exhibited round-like irregular-size nanoparticles (20-50 nm). PEDOT, similar to its SEM micrograph, was agglomerated through stacking, resulting in a micron-sized bulky topology. As observed in the SEM micrograph of the scaffold, the chemical incorporation of PCL to PEDOT caused a remarkable change that can be seen in the scaffold's TEM micrograph, disclosing a self-assembled micellar system containing spherical particles with scattered sizes.



Fig. 4 TEM micrographs of (a) PCL (b) PEDOT and (c) PEDOT-PCL scaffold.

Micellar systems are known to exist mostly in polymeric species containing both hydrophilic and hydrophobic moieties<sup>61</sup>. Nonetheless, both PEDOT and PCL are considered hydrophobic polymers<sup>62, 63</sup>. To investigate the hydrophobicity of all the synthesized polymers (PCL, PEDOT, and PEDOT-PCL), water contact angle measurements were conducted (Fig. 5).



Fig. 5 Water contact angle of PCL, PEDOT, and PEDOT-PCL scaffold.

PCL's water contact angle is 70.3°, as expected from a relatively hydrophobic polymer and this result is in close agreement with the literature. Surprisingly, the contact angle of PEDOT is 36.7°, which shows that the photochemically synthesized PEDOT showed hydrophilic behavior rather than hydrophobicity. The weak hydrophilicity is attributed to the dopant ions (bromide) present on PEDOT units, which can strongly interact with water molecules through ion-dipole interactions. This behavior was previously observed in studies regarding PEDOT: PSS (polystyrenesulfonate) due to the interaction of sulfonate ions with water molecules<sup>64</sup>. PEDOT-PCL's contact angle is calculated as 54.7°, which is between PCL and PEDOT's contact angles. The final wettability of the scaffold is ideal for most of the TErelated applications.

PEDOT-PCL scaffold displayed different colors in a variety of solvents. To understand the reason behind the solvatochromism, UV-vis absorbances and fluorescence emissions of the scaffold, in different solvents, were investigated. The above experimental results indicated the formation of statistical copolymers (PEDOT-ran-PCL) consisting of EDOT chains as strong electron donating groups and ECL chains with carbonyl as electron acceptor units which can result in an intramolecular charge transfer (ICT) property with a push-pull interaction. In order to inspect ICT in detail, PEDOT-PCL's solvatochromic behavior was investigated in eight different solvents, possessing different polarity indices, *i.e.* dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), ethanol (EtOH), acetone, tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), dichloromethane (DCM) and toluene. While the scaffold's UV absorption didn't change significantly in different solvents (Fig. S9), fluorescence emission spectra exhibited large bathochromic shifts (up to 144 nm shift) from toluene (509 nm) to DMF (653 nm) (Fig. 6), indicating a well stabilized excited state through the surrounding solvents with a strong ICT behavior and larger dipole moments compared to the ground state<sup>65-67</sup>. As previously concluded, the solvatochromism of absorption is unimportant in comparison to the bathochromic shift of the emission spectra<sup>68</sup>. However, a gradual shift was not observed from polar to nonpolar solvent as expected in any positive solvatochromism. The reason for the mixed solvatochromic behavior could be the self-assembling nature of PEDOT-PCL (Fig. 4), which results in specific interactions with the surrounding solvent molecules<sup>29</sup>.



**Fig. 6** (a) Fluorescence emission spectra of PEDOT-PCL in different solvents (b) Photos of PEDOT-PCL scaffold dissolved in different solvents (conc.:1 mg/ 1 mL).

Electroconductivities of PEDOT and PEDOT-PCL were measured using a four-point probe and calculated as 1.5 S/cm and 1.2 mS/cm, respectively. Scaffold's conductivity is higher than most of the previously fabricated PEDOT-PCL scaffolds. A drastic decrease in the electroconductivity of the scaffold, compared to that of PEDOT, is attributed to the presence of PCL units between PEDOT units. Subsequently, the electrochemical properties of PEDOT-PCL were examined by cyclic voltammetry (Fig. S10). HOMO and LUMO energy levels of the scaffold were calculated as -5.31 eV and -3.79 eV, respectively. Then, the electronic band gap was determined as 1.52 eV using  $E_{CV}$ = IHOMO-LUMOI equation. Interestingly, the band gap of PEDOT is also 1.52 eV. Cyclic voltammograms of PCL, in the literature, exhibited an irreversible oxidation peak at 1.1 V and a reduction potential at very low voltages (beyond – 2.0 V). Thus, the increase in the oxidation potential of PEDOT, is attributed to the incorporation of PCL. The HOMO/LUMO energy levels and electronic band gap of the polymer were found to be in good agreement with the band gaps of typical p-type conjugated materials<sup>69-71</sup>.

The crystallinity of the homopolymers and PEDOT-PCL scaffold was evaluated using PXRD (Fig. 7). Pristine PEDOT was totally amorphous exhibiting a broad peak centered at 20 = 24° corresponding to  $\pi$ - $\pi$  stacking of the aromatic units with a distance of d  $\approx$  4.5 Å<sup>72</sup>. Pristine PCL, on the other hand, exhibited a semi-crystalline character with two sharp peaks at 20 = 21.4° and 23.7°, which are assigned to (110) and (200) planes, respectively, and are in good agreement with the PCL literature<sup>73</sup>. While most of the previously synthesized PCL revealed almost pure crystalline character, photochemically synthesized PCL using DPIBr had a more amorphous character. This is due to decreased crystallinity of PCL with increasing molecular weight. Moreover, a slight shift can be observed in the powder diffractogram of PEDOT-PCL (Figure 4 inset) compared to PCL. This result also supports the chemical incorporation of PEDOT into PCL.



**Fig. 7** PXRD diffractograms of PCL, PEDOT, and PEDOT-PCL (inset graph is focused on 2 theta = 20-30°).

We then employed thermal analysis of PEDOT, PCL, and PEDOT-PCL scaffold using DSC (Fig. 8) and TGA (Fig. 9), respectively. Pristine PCL exhibited an endothermic peak at 63.4°C corresponding to the typical melting point ( $T_m$ ) of PCL<sup>74</sup>. PEDOT displayed a broad endotherm starting from 80°C. This is due to the removal of bromide ions from the polymer during heating and was previously encountered<sup>52</sup>. On the other hand, the PEDOT-PCL scaffold exhibited double melting points; one major endothermic peak at 53.7°C with a shoulder at 46°C. Such observation was previously reported and this shift to lower  $T_m$  was attributed to the chemical incorporation of PEDOT to PCL resulting in the formation of less crystalline material that melts at significantly lower temperatures<sup>28</sup>. Contrary to the PCL literature, during the cooling process, no glass transition was observed. This could be attributed to the semicrystalline nature of the synthesized PCL. According to the enthalpy found using DSC, the degree of crystallinity ( $X_c$ ) was calculated to be 15.7 from the following equation:  $X_c = (\Delta H^m / \Delta H^0) \times 100$  where  $\Delta H^m$  is the melting enthalpy and  $\Delta H_m$  is the fusion enthalpy of pure crystalline PCL with the value of 136 J/g (Fig S11)<sup>75</sup>.



**Fig. 8** (a) DSC thermograms of PCL, PEDOT, and PEDOT-PCL scaffold (b) focused on PEDOT and PEDOT-PCL endotherms.

The TGA result of pristine PEDOT (Fig. 10) reveals a significant weight loss until 150°C due to the removal of dopant ions (bromide), as such weight loss was previously observed in PEDOT produced by the same photoinduced step-growth polymerization<sup>52</sup>. After the removal of the dopant ions, PEDOT can be considered as thermally stable up until 400°C where a sudden weight loss occurs due to the thermal decomposition yielding 40% char. TGA thermogram of PCL exhibits the first 5% weight loss at 100°C due to possible evaporation of a trace amount of moisture and absorbed solvent. The melting point of PCL around 54°C can easily be observed in the differential thermal analysis (DTA) data (Fig. S12). Pristine PCL can be considered a stable polymer until 400°C, which is in agreement with the literature<sup>76</sup>. At 400°C, a sudden decomposition of PCL occurs which results in 0% char yield after 500°C. TGA of PEDOT-PCL scaffold reveals its thermal stability (first 5% weight loss) until 200°C. The higher thermal stability of PEDOT-PCL can be attributed to the decreased amount of bromide ions present in the scaffold since most of the HBr released is used for the ROP of ECL. Gradual weight loss occurs until 390°C where thermal decomposition of the scaffold starts yielding 20% char at 900°C. In short, the thermal stability of the photochemically fabricated PEDOT-PCL scaffold exhibits the average of the thermal stabilities of the two homopolymers (pristine PEDOT and PCL).



Fig. 9 TGA thermograms of PCL, PEDOT, and PEDOT-PCL scaffold.

## Conclusion

Fabrication of electroconductive nanoscaffolds plays a crucial role in tissue engineering. In this study, the PEDOT-PCL scaffold was fabricated for the first time, by an innovative light-induced *in situ* method which merges step-growth and chain-growth polymerizations. Results indicated that the scaffold contained ~30% PEDOT. SEM and TEM micrographs demonstrated the drastic changes in the morphology and topology of the scaffold, respectively. PEDOT-PCL displayed all the desired features of a TE scaffold including interconnected nanoporosity, low melting point, and high electroconductivity. Another advantage of the originated methodology is to avoid the use of sophisticated techniques such as electrospinning or vapor-phase polymerization. Furthermore, as a consequence of the self-assembling nature, the scaffold exhibited mixed solvatochromism which can be used in sensor applications.

## Acknowledgements

This paper is dedicated to the memory of our dear Professor Yusuf Yagci. The authors thank Zafer Eroglu, Tugser Yilmaz and Adalet Nur Altunkaya for their help in SEM, TEM, PXRD and water contact angle measurements. This work is supported by the Turkish Council of High Research (YOK) Project no: YAP-44404 and Istanbul Technical University Research Fund.

### References

- 1. J. Janata and M. Josowicz, Conducting polymers in electronic chemical sensors, *Nature Materials*, 2003, **2**, 19-24.
- 2. I. Sahalianov, S. K. Singh, K. Tybrandt, M. Berggren and I. Zozoulenko, The intrinsic volumetric capacitance of conducting polymers: pseudo-capacitors or double-layer supercapacitors?, *RSC Advances*, 2019, **9**, 42498-42508.
- 3. A. R. Murad, A. Iraqi, S. B. Aziz, S. N. Abdullah and M. A. Brza, Conducting Polymers for Optoelectronic Devices and Organic Solar Cells: A Review, *Polymers*, 2020, **12**, 2627.
- 4. M. R. Abidian, D. H. Kim and D. C. Martin, Conducting-Polymer Nanotubes for Controlled Drug Release, *Adv Mater*, 2006, **18**, 405-409.
- 5. M. Talikowska, X. Fu and G. Lisak, Application of conducting polymers to wound care and skin tissue engineering: A review, *Biosensors and Bioelectronics*, 2019, **135**, 50-63.
- 6. E. N. Zare, P. Makvandi, B. Ashtari, F. Rossi, A. Motahari and G. Perale, Progress in Conductive Polyaniline-Based Nanocomposites for Biomedical Applications: A Review, *Journal of Medicinal Chemistry*, 2020, **63**, 1-22.
- 7. S. Cui, J. Mao, M. Rouabhia, S. Elkoun and Z. Zhang, A biocompatible polypyrrole membrane for biomedical applications, *RSC Advances*, 2021, **11**, 16996-17006.
- 8. D. Mawad, K. Gilmore, P. Molino, K. Wagner, P. Wagner, D. L. Officer and G. G. Wallace, An erodible polythiophene-based composite for biomedical applications, *Journal of Materials Chemistry*, 2011, **21**, 5555-5560.
- 9. C. Boehler, Z. Aqrawe and M. Asplund, Applications of PEDOT in bioelectronic medicine, *Bioelectronics in Medicine*, 2019, **2**, 89-99.
- 10. W. Jeong, G. Gwon, J.-H. Ha, D. Kim, K.-J. Eom, J. H. Park, S. J. Kang, B. Kwak, J.-I. Hong, S. Lee, D. C. Hyun and S. Lee, Enhancing the conductivity of PEDOT:PSS films for biomedical applications via hydrothermal treatment, *Biosensors and Bioelectronics*, 2021, **171**, 112717.
- 11. O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren and X. Crispin, Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene), *Nat Mater*, 2011, **10**, 429-433.
- 12. M. Solazzo and M. G. Monaghan, Structural crystallisation of crosslinked 3D PEDOT:PSS anisotropic porous biomaterials to generate highly conductive platforms for tissue engineering applications, *Biomaterials Science*, 2021, **9**, 4317-4328.
- 13. A. G. Guex, J. L. Puetzer, A. Armgarth, E. Littmann, E. Stavrinidou, E. P. Giannelis, G. G. Malliaras and M. M. Stevens, Highly porous scaffolds of PEDOT:PSS for bone tissue engineering, *Acta Biomater*, 2017, **62**, 91-101.
- 14. A. Abedi, M. Hasanzadeh and L. Tayebi, Conductive nanofibrous Chitosan/PEDOT:PSS tissue engineering scaffolds, *Materials Chemistry and Physics*, 2019, **237**, 121882.
- 15. N. Fani, M. Hajinasrollah, M. Asghari Vostikolaee, M. Baghaban Eslaminejad, F. Mashhadiabbas, N. Tongas, M. Rasoulianboroujeni, A. Yadegari, K. Ede, M. Tahriri and L. Tayebi, Influence of conductive PEDOT:PSS in a hard tissue scaffold: In vitro and in vivo study, *Journal of Bioactive and Compatible Polymers*, 2019, **34**, 436-441.
- 16. J. Chen, Y. Fan, G. Dong, H. Zhou, R. Du, X. Tang, Y. Ying and J. Li, Designing biomimetic scaffolds for skin tissue engineering, *Biomaterials Science*, 2023, **11**, 3051-3076.
- 17. M. Peng, Q. Zhao, M. Wang and X. Du, Reconfigurable scaffolds for adaptive tissue regeneration, *Nanoscale*, 2023, **15**, 6105-6120.
- 18. A. Eltom, G. Zhong and A. Muhammad, Scaffold Techniques and Designs in Tissue Engineering Functions and Purposes: A Review, *Advances in Materials Science and Engineering*, 2019, **2019**, 3429527.
- 19. , The Design of Scaffolds for Use in Tissue Engineering. Part II. Rapid Prototyping Techniques, *Tissue Engineering*, 2002, **8**, 1-11.

- 20. H. Zhao, M. Liu, Y. Zhang, J. Yin and R. Pei, Nanocomposite hydrogels for tissue engineering applications, *Nanoscale*, 2020, **12**, 14976-14995.
- 21. Y.-F. Li, H. Gregersen, J. V. Nygaard, W. Cheng, Y. Yu, Y. Huang, M. Dong, F. Besenbacher and M. Chen, Ultraporous nanofeatured PCL–PEO microfibrous scaffolds enhance cell infiltration, colonization and myofibroblastic differentiation, *Nanoscale*, 2015, **7**, 14989-14995.
- 22. G. B. Tseghai, D. A. Mengistie, B. Malengier, K. A. Fante and L. Van Langenhove, PEDOT:PSS-Based Conductive Textiles and Their Applications, *Sensors (Basel)*, 2020, **20**.
- 23. S. Jadoun, U. Riaz and V. Budhiraja, Biodegradable conducting polymeric materials for biomedical applications: a review, *MEDICAL DEVICES & SENSORS*, 2021, **4**, e10141.
- 24. S. Amini, H. Salehi, M. Setayeshmehr and M. Ghorbani, Natural and synthetic polymeric scaffolds used in peripheral nerve tissue engineering: Advantages and disadvantages, *Polymers for Advanced Technologies*, 2021, **32**, 2267-2289.
- 25. A. Dominguez-Alfaro, E. Gabirondo, N. Alegret, C. M. De León-Almazán, R. Hernandez, A. Vallejo-Illarramendi, M. Prato and D. Mecerreyes, 3D Printable Conducting and Biocompatible PEDOT-graft-PLA Copolymers by Direct Ink Writing, *Macromolecular Rapid Communications*, 2021, **42**, 2100100.
- 26. P. A. Saeed, R. Shilpa and A. Sujith, A water-mediated approach for the preparation of conductive poly(3,4-ethylenedioxythiophene)-decorated poly(methyl methacrylate) microcomposites, *Materials Advances*, 2022, **3**, 3875-3884.
- 27. Y.-F. Zhang, M.-M. Guo, Y. Zhang, C. Y. Tang, C. Jiang, Y. Dong, W.-C. Law and F.-P. Du, Flexible, stretchable and conductive PVA/PEDOT:PSS composite hydrogels prepared by SIPN strategy, *Polymer Testing*, 2020, **81**, 106213.
- A. Dominguez-Alfaro, M. Criado-Gonzalez, E. Gabirondo, H. Lasa-Fernández, J. L. Olmedo-Martínez, N. Casado, N. Alegret, A. J. Müller, H. Sardon, A. Vallejo-Illarramendi and D. Mecerreyes, Electroactive 3D printable poly(3,4-ethylenedioxythiophene)-graft-poly(*c*-caprolactone) copolymers as scaffolds for muscle cell alignment, *Polymer Chemistry*, 2022, 13, 109-120.
- 29. A.-D. Bendrea, L. Cianga, G.-L. Ailiesei, E.-L. Ursu, D. Göen Colak and I. Cianga, 3,4-Ethylenedioxythiophene (EDOT) End-Group Functionalized Poly-ε-caprolactone (PCL): Self-Assembly in Organic Solvents and Its Coincidentally Observed Peculiar Behavior in Thin Film and Protonated Media, *Polymers*, 2021, **13**, 2720.
- 30. A.-D. Bendrea, L. Cianga, G.-L. Ailiesei and I. Cianga, Fluorescent EDOT-Functionalized Polyε-Caprolactone: Synthesis, Photophysical and Self-Assembling Properties in Organic Solvents and Its Serendipitously Noticed Behaviour in Protonated Media, *Proceedings*, 2021, **69**, 13.
- 31. Y. Hou, W. Wang and P. Bartolo, Investigation of polycaprolactone for bone tissue engineering scaffolds: In vitro degradation and biological studies, *Materials & Design*, 2022, **216**, 110582.
- 32. R. Dwivedi, S. Kumar, R. Pandey, A. Mahajan, D. Nandana, D. S. Katti and D. Mehrotra, Polycaprolactone as biomaterial for bone scaffolds: Review of literature, *J Oral Biol Craniofac Res*, 2020, **10**, 381-388.
- 33. X. Yang, Y. Wang, Y. Zhou, J. Chen and Q. Wan, The Application of Polycaprolactone in Three-Dimensional Printing Scaffolds for Bone Tissue Engineering, *Polymers*, 2021, **13**, 2754.
- A. G. A. Coombes, S. C. Rizzi, M. Williamson, J. E. Barralet, S. Downes and W. A. Wallace, Precipitation casting of polycaprolactone for applications in tissue engineering and drug delivery, *Biomaterials*, 2004, 25, 315-325.
- 35. A. Leroux, T. Ngoc Nguyen, A. Rangel, I. Cacciapuoti, D. Duprez, D. G. Castner and V. Migonney, Long-term hydrolytic degradation study of polycaprolactone films and fibers grafted with poly(sodium styrene sulfonate): Mechanism study and cell response, *Biointerphases*, 2020, **15**, 061006.
- H.-Y. Chen, H.-J. Fang, Y.-J. Chen, S. Hsu, Y.-C. Lai, H.-W. Ou, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, H. Chung, Y. Chen, T.-C. Huang and B. Wu, In situ formation of Sn(IV) catalyst with increased activity in ε-caprolactone and L-lactide polymerization using stannous(II) 2-ethylhexanoate, *Journal of Polymer Science A Polymer Chemistry*, 2012, **50**, 3286-3294.
- G. Jiang, I. A. Jones, C. D. Rudd and G. S. Walker, Mechanistic study of Sn(Oct)2-catalyzed εcaprolactone polymerization using Sn(Oct)2/BF3 dual catalyst, *Journal of Applied Polymer Science*, 2009, **114**, 658-662.
- K. Kaluzynski, J. Pretula, P. Lewinski, S. Kaźmierski and S. Penczek, Synthesis and Properties of Functionalized Poly(ε-caprolactone); Chain Polymerization Followed by Polycondensation in One Pot with Initiator and Catalyst in One Molecule. Synthesis and Molecular Structures, *Macromolecules*, 2022, 55, 2210-2221.

- 39. B. Kiskan and Y. Yagci, Synthesis and characterization of naphthoxazine functional poly(εcaprolactone), *Polymer*, 2005, **46**, 11690-11697.
- 40. Y. Xu, L. Wang, C. Chen, P. Huang, H. Dai, W. Jiang and Y. Zhou, Living Cationic Polymerization of ε-Caprolactone Catalyzed by a Metal-free Lewis Acid of Trityl Tetrafluoroborate, *Macromolecules*, 2023, **56**, 501-509.
- 41. D. Mecerreyes, R. Stevens, C. Nguyen, J. A. Pomposo, M. Bengoetxea and H. Grande, Synthesis and characterization of polypyrrole-graft-poly(ε-caprolactone) copolymers: new electrically conductive nanocomposites, *Synthetic Metals*, 2002, **126**, 173-178.
- 42. B. G. Molina, A. D. Bendrea, L. Cianga, E. Armelin, L. J. del Valle, I. Cianga and C. Alemán, The biocompatible polythiophene-g-polycaprolactone copolymer as an efficient dopamine sensor platform, *Polymer Chemistry*, 2017, **8**, 6112-6122.
- 43. K. I. Ritzau-Reid, C. D. Spicer, A. Gelmi, C. L. Grigsby, J. F. Ponder Jr., V. Bemmer, A. Creamer, R. Vilar, A. Serio and M. M. Stevens, An Electroactive Oligo-EDOT Platform for Neural Tissue Engineering, *Advanced Functional Materials*, 2020, **30**, 2003710.
- 44. N. Roberto, J. Dias, L. Piaia, J. P. Borges and C. R. Henriques, Electrospun Polycaprolactone Fibers Doped with 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and Poly(3,4ethylenedioxythiophene) for Neural Tissue Engineering, *Materials Proceedings*, 2022, **8**, 150.
- 45. M. Acosta, M. D. Santiago and J. A. Irvin, Electrospun Conducting Polymers: Approaches and Applications, *Materials*, 2022, **15**, 8820.
- 46. A. Kocaarslan, K. Kaya, S. Jockusch and Y. Yagci, Phenacyl Bromide as a Single-Component Photoinitiator: Photoinduced Step-Growth Polymerization of N-Methylpyrrole and N-Methylindole, *Angewandte Chemie International Edition*, 2022, **61**, e202208845.
- 47. T. Celiker, K. Kaya, S. Koyuncu and Y. Yagci, Polypyrenes by Photoinduced Step-Growth Polymerization, *Macromolecules*, 2020, **53**, 5787-5794.
- 48. K. Kaya, S. Jockusch and Y. Yagci, Mussel-Inspired Coatings by Photoinduced Electron-Transfer Reactions: Photopolymerization of Dopamine under UV, Visible, and Daylight under Oxygen-Free Conditions, *Macromolecules*, 2021, **54**, 5991-5999.
- 49. M. B. Bilgic, K. Kaya, N. Orakdogen and Y. Yagci, Light-induced synthesis and characterization of "Clickable" polyacrylamide hydrogels, *European Polymer Journal*, 2022, **167**, 111062.
- 50. J. J. Chung, H. Im, S. H. Kim, J. W. Park and Y. Jung, Toward Biomimetic Scaffolds for Tissue Engineering: 3D Printing Techniques in Regenerative Medicine, *Front Bioeng Biotechnol*, 2020, **8**, 586406.
- 51. S. Vijayavenkataraman, S. Kannan, T. Cao, J. Y. H. Fuh, G. Sriram and W. F. Lu, 3D-Printed PCL/PPy Conductive Scaffolds as Three-Dimensional Porous Nerve Guide Conduits (NGCs) for Peripheral Nerve Injury Repair, *Front Bioeng Biotechnol*, 2019, **7**, 266.
- 52. K. Kaya, A green and fast method for PEDOT: Photoinduced step-growth polymerization of EDOT, *Reactive and Functional Polymers*, 2023, **182**, 105464.
- 53. W. G. McGimpsey and J. C. Scaiano, Photochemistry of α-chloro- and α-bromoacetophenone. Determination of extinction coefficients for halogen–benzene complexes, *Canadian Journal of Chemistry*, 1988, **66**, 1474-1478.
- 54. S. Zhu, L. Wen, Y. Xiao and M. Lang, Poly(ε-caprolactone) with pH and UCST responsiveness as a 5-fluorouracil carrier, *Polymer Chemistry*, 2020, **11**, 5173-5180.
- 55. J. V. Crivello, Design and Synthesis of Photoacid Generating Systems, *Journal of Photopolymer Science and Technology*, 2008, **21**, 493-497.
- 56. A. Benkaddour, K. Jradi, S. Robert and C. Daneault, Grafting of Polycaprolactone on Oxidized Nanocelluloses by Click Chemistry, *Nanomaterials*, 2013, **3**, 141-157.
- 57. S. V. Selvaganesh, J. Mathiyarasu, K. L. N. Phani and V. Yegnaraman, Chemical Synthesis of PEDOT–Au Nanocomposite, *Nanoscale Research Letters*, 2007, **2**, 546.
- 58. K. Kaya, S. Koyuncu and Y. Yagci, Photoinduced synthesis of poly(N-ethylcarbazole) from phenacylium salt without conventional catalyst and/or monomer, *Chemical Communications*, 2019, **55**, 11531-11534.
- 59. K. Żółtowska, M. Sobczak and E. Olędzka, Novel Zinc-Catalytic Systems for Ring-Opening Polymerization of ε-Caprolactone, *Molecules*, 2015, **20**, 2816-2827.
- 60. N. Pircher, D. Fischhuber, L. Carbajal, C. Strauß, J.-M. Nedelec, C. Kasper, T. Rosenau and F. Liebner, Preparation and Reinforcement of Dual-Porous Biocompatible Cellulose Scaffolds for Tissue Engineering, *Macromolecular Materials and Engineering*, 2015, **300**, 911-924.
- 61. N. A. N. Hanafy, M. El-Kemary and S. Leporatti, Micelles Structure Development as a Strategy to Improve Smart Cancer Therapy, *Cancers (Basel)*, 2018, **10**.
- 62. M. Döbbelin, R. Marcilla, C. Tollan, J. A. Pomposo, J.-R. Sarasua and D. Mecerreyes, A new approach to hydrophobic and water-resistant poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) films using ionic liquids, *Journal of Materials Chemistry*, 2008, **18**, 5354-5358.

- 63. X. Qin, Y. Wu, S. Liu, L. Yang, H. Yuan, S. Cai, J. Flesch, Z. Li, Y. Tang, X. Li, Y. Zhuang, C. You, C. Liu and C. Yu, Surface Modification of Polycaprolactone Scaffold With Improved Biocompatibility and Controlled Growth Factor Release for Enhanced Stem Cell Differentiation, *Front Bioeng Biotechnol*, 2021, **9**, 802311.
- 64. M. Solazzo and M. G. Monaghan, Hydrophilic, conductive and flexible piezoresistive PEDOT:PSS 3D sensors with tunable microarchitecture and crosslinked using a PEGylated crosslinker, *Synthetic Metals*, 2022, **290**, 117157.
- 65. R. Isci, A. Rahimi Varzeghani, K. Kaya, B. Sütay, E. Tekin and T. Ozturk, Triphenylamine/Tetraphenylethylene Substituted 4-Thieno[3,2-b]thiophen-3-ylbenzonitriles: Synthesis, Photophysical-Electronic Properties, and Applications, *ACS Sustainable Chemistry* & Engineering, 2022, **10**, 1605-1615.
- 66. R. Isci, M. Unal, G. Kucukcakir, N. A. Gurbuz, S. F. Gorkem and T. Ozturk, Triphenylamine/4,4'-Dimethoxytriphenylamine-Functionalized Thieno[3,2-b]thiophene Fluorophores with a High Quantum Efficiency: Synthesis and Photophysical Properties, *The Journal of Physical Chemistry B*, 2021, **125**, 13309-13319.
- 67. R. Isci, L. Wan, S. Topal, D. Gunturkun, A. J. Campbell and T. Ozturk, Solution-processable donor–π–acceptor type thieno[3,2-b]thiophene derivatives; synthesis, photophysical properties and applications, *Journal of Materials Chemistry C*, 2022, **10**, 10719-10727.
- 68. A. Popczyk, Y. Cheret, A. El Ghayoury, B. Sahraoui and J. Mysliwiec, Solvatochromic fluorophores based on thiophene derivatives for highly-precise water, alcohols and dangerous ions detection, *Dyes and Pigments*, 2020, **177**, 108300.
- 69. R. Isci, D. Gunturkun, A. S. Yalin and T. Ozturk, Copolymers of 4-thieno[3,2-b]thiophen-3ylbenzonitrile with anthracene and biphenyl; synthesis, characterization, electronic, optical, and thermal properties, *Journal of Polymer Science*, 2021, **59**, 117-123.
- 70. R. Isci, T. Balkan, S. Tafazoli, B. Sütay, M. S. Eroglu and T. Ozturk, Thienothiophene and Triphenylbenzene Based Electroactive Conjugated Porous Polymer for Oxygen Reduction Reaction (ORR), *ACS Applied Energy Materials*, 2022, **5**, 13284-13292.
- 71. T. Celiker, R. İsci, K. Kaya, T. Ozturk and Y. Yagci, Photoinduced step-growth polymerization of thieno[3,4-b] thiophene derivatives. The substitution effect on the reactivity and electrochemical properties, *Journal of Polymer Science*, 2020, **58**, 2327-2334.
- 72. T. Ghosh, J. S. Panicker and V. C. Nair, Self-Assembled Organic Materials for Photovoltaic Application, *Polymers*, 2017, **9**, 112.
- 73. A. Wibowo, C. Vyas, G. Cooper, F. Qulub, R. Suratman, A. I. Mahyuddin, T. Dirgantara and P. Bartolo, 3D Printing of Polycaprolactone–Polyaniline Electroactive Scaffolds for Bone Tissue Engineering, *Materials*, 2020, **13**, 512.
- 74. M. Nairn, DOI: 10.13140/RG.2.2.12743.80803, 2010.
- 75. E. Kuzelova Kostakova, L. Meszaros, G. Maskova, L. Blazkova, T. Turcsan and D. Lukas, Crystallinity of Electrospun and Centrifugal Spun Polycaprolactone Fibers: A Comparative Study, *Journal of Nanomaterials*, 2017, **2017**, 8952390.
- 76. L. M. Lozano-Sánchez, I. Bagudanch, A. O. Sustaita, J. Iturbe-Ek, L. E. Elizalde, M. L. Garcia-Romeu and A. Elías-Zúñiga, Single-Point Incremental Forming of Two Biocompatible Polymers: An Insight into Their Thermal and Structural Properties, *Polymers*, 2018, **10**, 391.