Aggregation and thermally induced photo-physics and structural ordering of thiophene-quinoxaline copolymer

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Abstract
Aggregation and thermally induced photo-physics of a low band gap thiophene-quinoxaline copolymer (TQ1) was investigated. The S0 → S1 transition of TQ1 in solution is found to be due to an intra-molecular charge transfer state while the excited state in aggregated TQ1 chains was due to intra and inter-chain excitons. On the other hand, the emission of TQ-1 recorded at 85 °C for more than 300 h confirmed that thermal stress hampers the inter-chain interaction as confirmed by the disappearance of the vibronic shoulder ascribed to it in the PL. In addition, it was observed that the PL intensity has drastically decreased while its absorption showed smaller change due to annealing for less than 40 h which confirmed either the introduction of new non-radiative channels or coiling of the copolymer due to thermal stress. The evolution XRD traces of TQ1 with thermal stress confirmed that it takes higher energy to break the long-range order than the molecular bonds in the copolymer.

1. Introduction
The emergence of π-conjugated semiconducting polymers has brought forth the era of organic electronics among which, organic solar cells (OSCs) have been widely studied in the past three decades. The main research directions on OSCs research include the synthesis of polymers with appropriate energy level and planar backbone structure that facilitates charge transport and device fabrication geometry. A large number of polymers have been introduced to fabrication OSCs and the effort has paid back that now efficiencies above 18% and 17% in single and multi-junction devices have been achieved, respectively [1, 2]. The copolymerization of electron deficient units with electron rich units in donor-acceptor copolymers is the main synthetic route to produce low band gap polymers that has an absorption that extends to the near-infrared region of the solar spectrum. Among the many acceptor units introduced to the synthesis of donor-acceptors copolymers, a quinoxaline acceptor unit is rapidly being used as a strong electron withdrawing unit due to the two N atoms at the 1,4 positions. The first OSCs using using quinoxaline based copolymer attained a PCE of 3.7% [3]. A subtle modifications in the backbone structure of the quinoxaline based copolymers has become an promising route to produce highly performing OSCs that in less than 10 years PCEs exceeding 8% and a remarkable PCE of 11.34% were obtained [4, 5].

The understanding of photophysics of π-conjugated polymers is vital for further optimization of the structure of the existing polymers for better performing OSCs. This includes the photophysics of standalone polymer chains and aggregates of several chains. Recently, aggregation of polymers in solutions has been studied intensively due to its direct implication on the film organization of the materials upon fabrication of OSCs [6–9]. Moreover, the formation of aggregates is essential for a good charge transport in OSCs due to an improved inter-chain interaction. The aggregation of polymer chains in solution can easily be determined using UV-Vis absorption and fluorescence spectroscopy [10, 11]. The interaction of the chains in aggregated π-conjugated polymers shifts the energy level of the aggregate which splits the excited state energy level [11]. Consequently, a new aggregation dictated photo-physics will govern the exciton/charge dynamics in the polymers. During aggregation, depending on the interaction of dipoles of the polymer chains, two types (H and J) of aggregation...
will occur. In the case of parallel dipoles, H aggregates, the lower transition will be dipole forbidden while an efficient transition from the lower state is expected in head-to-tail arranged dipoles, J aggregates.

Besides the photo-physics of polymers, their stabilities are determining factors for the industrialization of organic electronics technology. Degradation of polymers can be caused due to several factors that include light exposure and elevated temperatures. Solar cells working under continuous illumination gets heated up above the temperature of the environment. Hence, OSCs will suffer from thermally-induced degradation due to the prolonged light exposure which makes thermal stability of polymers of paramount importance to ensure the stability of the technology. The thermal stability of polymers has to be tested at a temperature of 85 °C according to American Society for Testing and Materials (ASTM) E-1171 to be certified as thermally stable [12].

In this work, the effect of aggregation and annealing on the photo-physics of quinoxaline-thiophene (TQ1) copolymer. TQ1 is an alternating copolymer based on an alkoxylated quinoxaline acceptor and a thiophene donor is reported. The PCE of TQ1 based OSCs has been reported to be over 5% by Wang et al [13]. Its photochemical stability was also investigated [14, 15]. The photo-physics and structural ordering of copolymers during annealing is important to determine its stability under high thermal stress. Hence in this work, the thermal stability of TQ1 was investigated by monitoring the evolution of its PL and x-ray diffraction (XRD)-traces. Finally, the thermal property of TQ1 was investigated to assist the analysis of its thermal stability.

2. Experimental section

2.1. Optical characterization
Absorption spectra of TQ1 are taken both in film and solutions using Perkin Elmer Lambda 19 UV-VIS/NIR spectrophotometer. The solvents used were chloroform (CF) and 1,2-dichlorobenzene (oDCB) with polarity indices of 4.1 and 2.7, respectively. Similarly, the photoluminescence (PL) spectra of the copolymer were recorded in film and solutions using JY Horiba, Fluoromax-4 spectrofluorometer.

2.2. Thermal properties
The thermal properties of TQ1 was investigated using DTG-60H thermogravimetric analyser (TGA) in a temperature range from room temperature to 800 °C. The measurement was recorded under nitrogen atmosphere in platinum crucible at a heating rate of 15 °C/min.

2.3. Powder x-ray diffraction
The x-ray diffraction (XRD) traces of drop cased film of TQ1 from CF solution on glass substrate was recorded using Shimadzu Scientific Instruments x-ray diffractometer-7000S for 2θ values of between 2 to 40°. The diffractometer is fitted with Cu-Kα radiation and gun of power 40 kV × 40 mA with Cu target. XRD traces of TQ1 were recorded for fresh and thermally degraded films at different heating time intervals and the interlayer spacing is calculated using Bragg’s law equation (1).

\[ n\lambda = 2d \sin \theta \]  

where \( n \), \( \lambda \), and \( \theta \) are order of diffraction (1), wavelength of the x-ray (0.154 nm), and angle of diffraction, respectively.
2.4. Density functional theory calculations
Density functional theory (DFT) calculation was performed on TQ1 monomeric structure using gaussian 09 software with B3LYP hybrid functional and 6-31G* basis set. Geometry optimizations and molecular energy levels calculations were executed. The aloxy side chains are replaced by a single methoxy unit to reduce computational time as recommended in different reports [16, 17].

3. Result and discussion

3.1. Optical spectroscopy
The absorption spectra of TQ1 in film and CF solution together with its chemical structure are shown in figure 1(a). Its absorption spectra in films and solution have two dominant peaks at 596 and 358 nm and at 362 and 620 nm, respectively. The two-bands absorption profile of TQ1 is common in copolymers. The high energy band is due to $\pi - \pi^*$ transition while the low energy band is due to intramolecular charge transfer (ICT) between the donor thiophene and the acceptor quinoxaline units. The absorption spectra of TQ1 both in film and solution do not exhibit any vibronic shoulder indicating the copolymer is quite flexible and non-planar in its ground state [11]. The ICT transition in TQ1 film is red-shifted by 24 nm from its spectrum in solution indicating a good $\pi - \pi$ stacking due to improved inter-chain interactions upon solidification of the copolymer. Moreover, the absorption of TQ1 in film is broader and a band gap of 1.68 eV is calculated from the onset. The optical parameters of TQ1 are summarized in table 1.

The PL of TQ1 in film was found to be Stoké's-shifted by 160 nm and reveal vibronic shoulder indicating the presence of other convoluted bands as shown in figure 1(b). The deconvolution of the PL spectra revealed two deactivation channels in the solid which are the intra- and inter-chain exciton emitting at 780 and 847 nm, respectively [18]. Unlike the PL of TQ1 in film, its spectra in CF dilute solution does not show a vibronic shoulder due to the absence of an inter-chain interaction in the dilute solution that absorbs below 0.1 as shown in figure 2 (red broken lines). However, this emission can be either from the tightly bound intra-chain exciton or ICT state.

In order to investigate the property of the first excited state of TQ1 stand-alone chains, its PL spectra were recorded in two solvents of different polarity (i.e. oDCB (2.7) and CF (4.1)) and the result is shown in figure 2 (broken lines). The PL was found to be red-shifted with increasing solvent polarity by 13 nm confirming the dipolar characteristics the first excited state which is common in copolymers due to ICT between the donor and

![Figure 2. Absorption (solid lines) and PL (broken lines) spectra of TQ1 in CF (red) and oDCB (black).](image)

| Copolymer | 2cAbs Max (nm) | 2cPL | $E_{opt}'$ (eV) | stokes Shift |
|-----------|----------------|------|-----------------|-------------|
| TQ1       |                |      |                 |             |
| Film      | 362            | 620  | 780             | 160         | 1.68        |
| CF soln   | 358            | 597  | 722             | 125         | -           |
| DCB Soln  | 355            | 600  | 709             | 109         | -           |

Table 1. Optical parameters of TQ1.
acceptor moieties. Moreover, the PL spectra of TQ1 in oDCB is found to be narrower and reveal a weak shoulder around 780 nm implying the presence of another excited state. On the other hand, the absorption of TQ1 in CF and oDCB solvents showed negligible shift with increasing solvent polarity indicating the non-polar characteristics of the ground state [19].

3.2. Effect of aggregation on photo-physics of TQ1

The first electronically excited state in polymers is a band of a Wannier-Mott type intra-chain exciton. However, in aggregated polymer films a Frenkel type inter-chain exciton also exist due to the interaction with neighbouring polymer chains which plays an important role in charge dynamics of organic electronic devices. The aggregation of polymer chains in solution is found to determine the subsequent phase separation of donor and acceptors in OSCs’ active layer [20, 21]. This motivated us to study the optical properties of TQ1 in good/poor (CF/methanol) mixed solvent that can induce aggregation due to a significantly lower solute-solvent interaction that forces the polymer chains to approach each other [11]. The absorption of TQ1 in CF:methanol mixed solvent is found to be red-shifted with increasing methanol concentration which indicates the formation of J-aggregate in the solution [11, 22, 23]. There was no significant broadening of the spectra that would indicate the formation of both H and J-aggregates formation as shown in figure 3. The emission of TQ1 in the mixed solvents was recorded at excitation of 600 nm to further elucidate the aggregate formation in the copolymer and is depicted in figure 4. The PL spectrum of TQ1 was found to be red shifted and significantly quenched with increasing methanol concentration in the mixed solvent. The red shift in fluorescence of TQ1 as the methanol
content increases is attributed to the J-aggregates formed by the head-to-tail orientation of polymer chains [11]. The suppression of H-aggregates formation in TQ1 might be due to the long aloxy side chains that do not favour the formation of parallel aggregates. The J-aggregates formation improves the radiative recombination of the excitonic state which is important for efficient light emitting diodes [24, 25].

In addition, a vibronic shoulder above 850 nm was observed to appear in the PL spectrum of TQ1 with increasing methanol concentration. Interestingly, the PL spectra evolves from a mirror image of its absorption in the pure CF to a vibronically structured spectra in the mixed CF: Methanol solvent. The progressively evolved non-mirror image PL spectrum indicates different origins of the absorption and PL spectra in aggregated TQ1 chains [26]. To ascribe this newly evolved state, the normalized PL of TQ1 in pure CF, 20:80 CF: Methanol, and film are compared as shown in figure 4(b). The similarity of the PL spectra profiles of TQ1 in 20:80 CF: Methanol and film indicates that the emission at 850 nm in the mixed solvent is due to inter-chain exciton. The ICT population in aggregated polymer chains must be impaired due to the inter-chain exciton generation which consequently will red-shift the PL and change its profile as shown in figure 3(b). This led to a conclusion that in the presence of aggregates the inter-system conversion from the tightly bound excitonic to ICT state is reduced due to an improved interchain interaction which might be faster than the intra-chain dynamics [19]. The good interchain interaction in the copolymer aggregates is beneficial for charge transport [21].

In summary, the photo-physics of a single polymer chain is mainly explained by a Wannier-type Exciton → ICT formation. However, the photo-physics of TQ1 in aggregates is modelled as follows; incident photons on TQ1 creates Wannier-Mott type exciton which will relax to either intra-chain exciton or Frenkel type inter-chain exciton. Note here the Wannier-type exciton relaxation is determined by the orientation of dipole moments of the polymer chains in the excited and ground states.

3.3. Effect of annealing on Emission and XRD traces of TQ1
The evolution of PL spectrum of TQ1 film with annealing time is recorded as shown in figure 5(a). The PL spectrum of the fresh TQ1 film reveals a vibronic shoulder which disappears with increasing annealing time. Moreover, the main peak (0–0 transition) is red shifted with annealing as shown in the inset of figures 5(a) and (b)(black). The loss in PL intensity is fast that more than 50% of the emission is lost in less than 40 h while its absorption showed a negligible loss as depicted in figure 5(b) in green and inset, respectively. The high PL loss in the first 40 h therefore should be due to the introduction of a quenching state or non-radiative recombination in the copolymer which can be due to coiling of the polymer chains by the thermal stress [27]. In addition, the disappearance of the vibronic shoulder and narrowing of the PL spectrum of TQ1 with increasing annealing time indicates the aggregate formation in the film is not favoured with high thermal stress (see figure 5(a)). Finally, the PL spectrum is completely bleached above 100 h of annealing due to the thermally-induced degradation of the co-polymer.

The XRD trace of fresh TQ1 drop casted films reveal a sharp peak and a broad halo at 2θ = 3.52 and 23.02°, respectively. The small-angle diffraction peak corresponds to an ordered lamellar (100) planes that are separated by the aloxy side chain with an inter-lamellar distance of 2.51 nm. On the other hand, the broad featureless peak (010) is due to π − π inter-chain stacking of TQ1 chains corresponding to a π-stack distance of 0.38 nm. The XRD traces of TQ1 film was monitored for more than 300 h of heating at a temperature of 85 °C to interrogate
thermally-induced structural ordering changes. The diffraction trace of degraded TQ1 films are similar to the fresh film. However, the intensity of the small angle diffraction peak has increased by more than two fold upon annealing for more than 300 h indicating an improved alignment of polymer chains with thermal stress. The high angle diffraction peak on the other hand did not show any significant intensity change or diffraction angle shift.

The thermal degradation of TQ1 starts as early as 5 h as shown in the inset of figure 5(b). In addition, different researchers confirmed bond breaking of TQ1 copolymer starts below 20 h of heating [14]. However, the XRD traces of TQ1 recorded after annealing (figure 6) shows that the material keeps it order for more than 300 h. A similar result was obtained in our last work that is submitted for publication. These results clearly show that the degradation of long-range order in TQ1 takes more energy than breaking the molecular bonds [28].

3.4. Thermo-gravimetric analysis of TQ1
The thermal properties of TQ1 were investigated using TGA under nitrogen atmosphere. The thermal decomposition temperature ($T_D = 5\%$ mass loss) of the copolymer was found to be 410 °C. This high decomposition temperature ensures the applicability of the co-polymer in high temperature processing organic electronics techniques such as roll-to-roll printing.

The DTG curve, shown in dark yellow in figure 7, depicts two peaks indicating that the decomposition of TQ1 occurs in a two-step process. The rates of degradations of these two steps attain their maximum values at
474 and 633 °C, corresponding to a remaining mass of 82 and 36%, respectively. The first decomposition process of TQ1 corresponds to a small mass loss of 18% which suggests that this process is mainly the breaking of the aloxy side chains. Hence, the decomposition of TQ1 starts with the aloxy side chains breaking followed by the main backbone structure volatilization. After all the decomposition processes have taken place, a 10% residual mass at 700 °C is left.

3.5. Background geometry and frontier orbitals of TQ1

The backbone geometry of a π-conjugated polymer plays a crucial role in its charge transport characteristics. The optimized ground state background geometry of TQ1 is calculated using DFT with B3LYP/G-19 basis set as shown in figures 8(a) and (b). The backbone structure of TQ1 is found to be twisted that the thiophene ring is out by more than 28° from the plane of pyrazine ring. This is in agreement with its absorption profile that revealed no shoulder (see figure 1(a)). The non-planar geometry of the copolymer might hinder its charge mobility when used in organic electronics [29].

The frontier molecular orbitals of a given polymeric material determines its optoelectronic properties that subsequently determine its applications. The HOMO and LUMO levels of TQ1 were calculated to be −5.77 and −2.88 eV using B3LYP level with G-31 basis set. The HOMO-LUMO gap (2.89 eV) was found to be higher that the experimentally obtained value i.e HOMO = −5.4 eV and LUMO = −3.4 eV [14]. This discrepancies are expected because of the single number of monomer units considered in the calculation unlike the polymer which is composed of several units. The electron cloud distribution in the HOMO and LUMO is similar that it spread along the pyrazine and thiophene units implying a strong donor-weak acceptor coupling in TQ1 as shown in figure 8(c) and d. Such molecular orbital distribution affects the ICT and electron transfer characteristics of TQ1 to the acceptor units when used in an OSCs since hopping processes is hindered when the electron density is delocalized [30–32]. In addition, it worth noting that there is no electron cloud in the benzene rings indicating that they do not contribute to the π-electron density in the copolymer.

4. Conclusion

The effects of aggregation and annealing on the photo-physics of thiophene-quinoxaline copolymer (TQ1) were studied. The copolymer revealed an absorption profile with no vibronic structure indicating its non-planar backbone geometry. The DFT calculation also confirmed that the thiophene ring is 28° out of the plane of the pyrazaine ring. The emission of the copolymers was found to be from depopulation of ICT state in the absence of inter-chain interaction as confirmed by solvent-polarity dependent PL measurement. However, the PL of TQ1 in aggregated films was found to be red-shifted and revealed two deactivation channels, which were ascribed to intra and inter-chain exciton relaxation. An increase in the red-shift of PL of TQ1 in mixed solvent was observed.
with the increase of the poor solvent concentration confirming the formation of J-aggregates. The TQ1 film was annealed for more than 300 h to understand thermally-induced photophysics on TQ1 films. The PL intensity decreases by more than 50% despite the small decrease in absorbance indicating the PL is quenched due to coiling of the copolymer chains that traps charge carriers or due to the generation of a non-radiative recombination channel. The vibronic shoulders in the PL disappeared with increasing thermal stress which confirms that annealing does not favour aggregation in TQ1. The structural ordering in TQ1 investigated by XRD indicated that molecular ordering in the copolymer needs higher energy to break than the molecular bonds.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Cui Y et al 2020 Adv. Mater. 32 1908205
[2] Meng L et al 2018 Science 361 1094–8
[3] Gadisa A, Mammo W, Andersson L M, Admassie S, Zhang F, Andersson M R and Ingana O 2007 Adv. Funct. Mater. 17 3836–42
[4] Kim Y, Yeom H R, Kim J Y and Yang C 2013 Energy & Environmental Science 6 1909–10
[5] Zheng Z, Awaratani O M, Gautham B, Liu D, Qin Y, Li W, Bataller A, Gundogdu K, Ade H and Hou J 2017 Adv. Mater. 29 1604241
[6] Zhang T et al 2021 Journal of Energy Chemistry 59 30–7
[7] Wang T and Bredas J L 2011 Journal of the American Chemical Society 133 1822–35
[8] Qin Y, Zhang S, Xu Y, Ye L, Wu Y, Kong J, Xu B, Yao H, Ade H and Hou J 2019 Adv. Energy Mater. 9 1901823
[9] Schubert M et al 2012 Adv. Energy Mater. 2 369–80
[10] Zhao X, Sun P and Zhao K 2021 Helijon 7 e06638
[11] Bellelette M, Bouchard J, Leclerc M and Durocher G 2005 Macromolecules 38 880–7
[12] ASTM 2019 International Standard for Material Testing ASTM E 15 1171
[13] Wang E, Hou L, Wang Z, Helström S, Zhang F, Ingana O and Andersson M R 2010 Adv. Mater. 22 5240–4
[14] Henriksson P, Lindqvist C, Abdisa B, Wang E, George Z, Kroon R, Müller C, Yohannes T, Ingana O and Andersson M R 2014 Sol. Energy Mater. Sol. Cells 130 138–43
[15] Carlé J E, Jørgensen M, Manceau M, Helgesen M, Hagemann O, Sendergaard R and Krebs F C 2011 Sol. Energy Mater. Sol. Cells 95 3222–6
[16] Hlei E, Mbarek M, Gouid Z, Romdhane S, Said R B, Guesmi M, Egbe D and Bouchriha H 2020 J. Phys. Chem. Solids 136 109157
[17] Ma Z, Geng H, Wang D and Shuai Z 2016 J. Mater. Chem. C 4 4546–55
[18] Yamagata H and Spano F C 2012 J. Chem. Phys. 136 184901
[19] Tegegne N A, Abdisa Z, Mammo W, Andersson M R, Schlettwein D and Schwoerer H 2018 J. Polym. Sci., Part B: Polym. Phys. 56 1475–83
[20] Jung J, Lee W, Lee C, Ahn H and Kim J 2016 Adv. Energy Mater. 6 1600504
[21] Zhang L, Ding Z, Zhao R, Jiriu F, Ma W, Liu J and Wang L 2020 Journal of Materials Chemistry C 8 5613–9
[22] Tay-Agboso S, Street S and Kipert L D 2018 J. Photochem. Photobiol., A 362 31–9
[23] Spano F C and Silva C 2014 Annu. Rev. Phys. Chem. 65 477–500
[24] Dimitrov S D et al 2015 Nat. Commun. 6 1–8
[25] Minaev B, Baryshnikov G and Agren H 2014 Phys. Chem. Chem. Phys. 16 1719–58
[26] Gallaher J K, Chen K, Huff G S, Prasad S K, Gordon K C and Hodgkiss J M 2016 The Journal of Physical Chemistry Letters 7 3307–12
[27] Wang R, Yang X, Hu S, Zhang Y, Yan X, Wang Y, Zhang C and Sheng C 2019 The Journal of Physical Chemistry C 123 11055–62
[28] Aramini M, Niskanen J, Cavallari C, Pontioli D, Musazay A, Krisch M, Hakala M and Huotari S 2016 Phys. Chem. Chem. Phys. 18 5366–71
[29] Tanaka H, Wakamatsu A, Kondo M, Kuroda S, Kuroda S I, Shimoy Y, Park W T, Noh Y Y and Takenobu T 2019 Communications Physics 2 1–10
[30] Tegegne N A, Wendimu H, Abdisa Z, Mammo W, Andersson M R, Hone F G, Andoshee D M, Olaoye O and Bosman G 2020 J. Mater. Sci., Mater. Electron. 31 21303–15
[31] Tegegne N A et al 2020 The Journal of Physical Chemistry C 124 9644–55
[32] Kronemeijer A J, Gili E, Shahid M, Rivnay J, Salleo A, Heeney M and Sirringhaus H 2012 Adv. Mater. 24 1558–65