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Low-band gap and fluorescent poly(triphenylamine-thiazolo[5,4-*d*]thiazole) copolymer dye

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This study describes the synthesis, spectroscopy and band gap energy of new poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) dye. The p-TPTT polymer was examined by GPC, ^{1}H-NMR, FT-IR, UV-*vis*., fluorescence, thermal analysis (TA) and cyclic voltammetry (CV). It was found that the p-TPTT has a weigh average molecular weight (M_w) of 3596 and it has a good solubility in many organic solvents. The TA results showed that the p-TPTT is a stable polymer up to 400-500 °C. The E_g^{Opt} of the polymer was found as 1.85 eV in DMSO and 1.55 eV in solid phase. From the CV measurements, the HOMO and LUMO of the p-TPTT were obtained as -5.32 and -3.96 eV, respectively and the E_g^{CV} was measured as 1.36 eV. The p-TPTT exhibited fluorescence emissions at 500 and 522 nm. These results showed that the p-TPTT is a fluorescent and low band gap energy dye material for possible applications in LEDs and solar cells.

Introduction

The synthesis, electronic, optical and material properties of triarylamines have been studied by many researchers.[1,2] Triphenylamine (N,N-diphenylaniline) (TPA) molecule contains a single nitrogen atom and three phenyl groups (Fig. 1a). The redox activity and fluorescence behaviors of TPA derivatives are observed due to the high oxidisability of the nitrogen center and the transportability of positive charge centers via the radical cation species.[3] Therefore, triphenylamines including small molecules, dendrimers, star-shape compounds and polymers have been considered as an interesting organic semiconductor materials because of their electron-donating capability and good hole-transporting ability. Also, they have been widely utilized for donor-acceptor type applications in organic photovoltaics (OPVs).[3,4] As organic hole-transporting materials, triphenylamines have been received increasing attention in electro-optical devices, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and photorefractive holographic materials.[3]

The electro-optical, hole-transporting and fluorescence properties of TPA containing molecules or polymers have been examined by different researchers. For instance, triphenylamine-thiophene molecules,[4] poly(4-alkyltriphenylamine),[5] poly(triphenyl-amine), branched poly(triphenylamine),[6] poly(triphenylamine-amide),[7] poly(4-metoxyphenyl-amine)[8] and triphenylamine-fluorene,[9] have been reported. These polymers have relatively low band gap energies.

Thiazolo[5,4-*d*]thiazole is a bicyclic aromatic molecule with two fused thiazole rings containing electron donor N and S atoms (Fig. 1b).[10-12] The first compound of this class was prepared in 1891 by Ephraim,[13] but its correct structure was established only in 1960 by Johnson et al.[14-16] The potential biological activity, semiconductivity and solar cell material properties of thiazolo[5,4-*d*]thiazoles have been investigated.[16,17] New polymeric thiazolo[5,4-*d*]thiazole derivatives, for example, thiophene-thiazolo[5,4-*d*]thiazole,[18] thiophene-thiazolo[5,4-*d*]thiazole-naphthalene,[19,20] bithiophene-co-thiazolo[5,4-*d*]thiazo-le,[21] 2,5-dithienyl-thiazolo[5,4-*d*]thiazole[22] copolymers have been reported. Also, the thiazolo[5,4-d]thiazole containing copolymers are utilized as donor materials in polymer solar cells.[23-33] In our previous work, we have studied the band gap energy and the fluorescence spectroscopy and doping of poly(phenylene-thiazolo[5,4-*d*]thiazole) copolymer.[11,12]

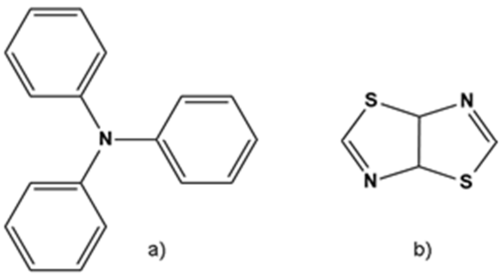

Fig. 1. a) Triphenylamine (TPA) b) Thiazolo[5,4-*d*]thiazole unit.

New electron donating and accepting groups bonded to thiazolo[5,4-*d*]thiazole unit are expected to change the electronic, spectroscopic and dye properties. Although different TPA and thiazolo[5,4-*d*]thiazole derivatives have been examined in the literature, a polymer containing only TPA and thiazolo[5,4-*d*]thiazole units, has not been prepared. In this study, a fully conjugated and alternating copolymer with TPA and thiazolo[5,4-

d]thiazole units, poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) copolymer, has been synthesized by the reaction of 4,4'-diformyltriphenylamine and rubeanic acid. The spectroscopy, voltammetry and thermal stability of the synthesized p-TPTT have been examined. The HOMO, LUMO and the band gap energies of the p-TPTT were also calculated from the UV-*vis*. absorption spectroscopy and the voltammetric measurements.

Results and discussion

Some triphenylamine-thiazolo[5,4-*d*]thiazole copolymers with thiophene and metoxy moieties have been examined.[16] In our previous work, the synthesis of a thiazolo-thiazole conjugated copolymer, poly(phenylene-thiazolo[5,4-*d*]thiazole (p-PhTT), was performed by the reaction between terephtalaldehyde and rubeanic acid.[11,12] However, a polymer consisting of triphenylamine and thiazolo[5,4-*d*]thiazole has not been studied. In this perspective, here, poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) has been synthesized by the reaction of 4,4'-diformyltriphenylamine and rubeanic acid. The p-TPTT copolymer was specially designed to include conjugated triphenylamine and thiazolo[5,4-*d*]thiazole units. The synthesis reaction and the chemical structure of the p-TPTT alternating copolymer are given in Fig. 2.[11,12] The prepared polymer is a dye material with two chromophoric light absorbing groups. As a chromophoric group, the triphenylamine has tert-aromatic amine with n electrons and three phenyls with π electrons. Similar to many N containing polymers,[35] the light absorbing thiazolo[5,4-*d*]thiazole group includes n electrons of N and S hetero atoms together with the π electrons,.[11,12,35]

After the preparation of the p-TPTT copolymer, the dissolution of the polymer powder was examined in different solvents. It was determined that the p-TPTT polymer is soluble in DMSO, CH_3CN, acetone, toluene, $CHCl_3$ and THF. The solubility of the polymer in these six solvents is an important advantage for the physical processing of the dye material. During the preparation of thin film coatings, solvent casting, spin coating and deep coating processing methods requires soluble dye materials. The p-TPTT copolymer was examined by using GPC, UV-*vis*. absorption, FT-IR, fluorescence, NMR, thermal and voltammetric methods.

GPC molecular weight

The molecular weight of the p-TPTT polymer was found as M_n and Mw values from the GPC measurements. The THF solution of the p-TPTT was used in the measurements. The obtained molecular weight fraction results are given in Fig. 3. According to the GPC experiments, the p-TPTT has a weigh average molecular weight (M_w) of 3596 and a number average molecular weight (M_n) of 2552 with n = 9-10.

FT-IR spectroscopy

The FT-IR spectra of the 4,4'-diformyltriphenylamine (DPA) and rubeanic acid monomers used in the polymerization and the HCl doped and undoped p-TPTT copolymer samples were measured for the characterization. The obtained FT-IR spectra are given in Fig. 4. Some important changes in the FT-IR measurements have been noted. For example, the primary amine peaks of rubeanic acid between 3000 and 3400 cm^{-1} wavenumbers disappeared in the spectra of the polymer samples. The peaks at 3000- 3400 cm^{-1} in the FT-IR spectra of HCl doped p-TPTT polymer sample attributed to protonated amines.

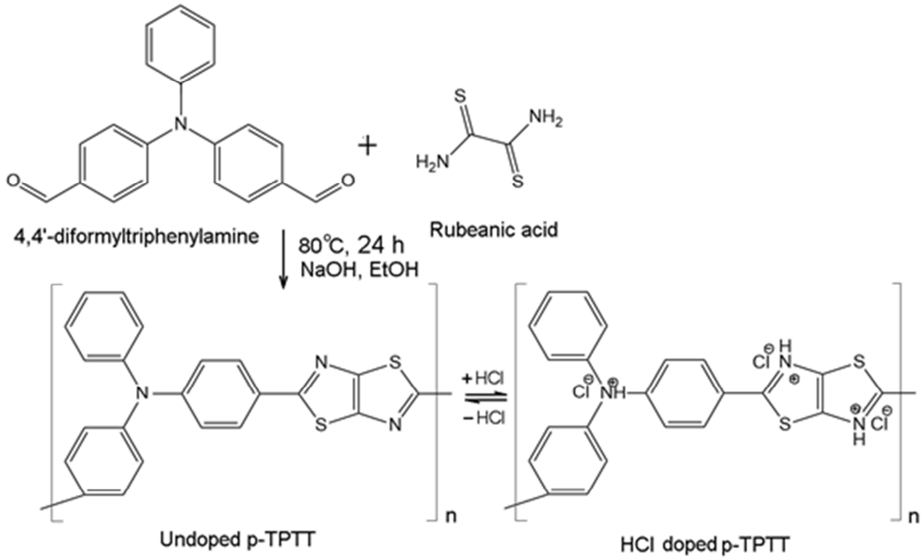

Fig. 2. Synthesis and HCl doping of poly(triphenylamine-thiazolo[5,4-*d*]thiazole) copolymer.

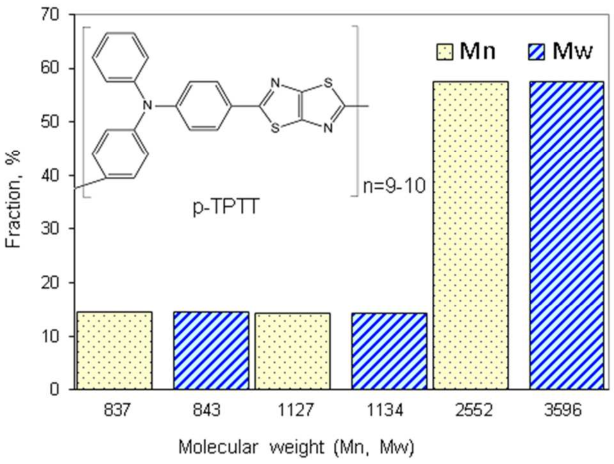

Fig. 3. Molecular weight fractions of p-TPTT.

In addition, the peaks at 3000-3400 cm^{-1} in the spectra of the undoped p-TPTT polymer disappeared because of the lack of N-H peaks. The peak at 1687 cm^{-1} in the spectrum of DPA was attributed to the C=O vibration of the aldehyde group of the DPA and its intensity decreased in the spectra of the p-TPTT polymer sample. The residual peak at 2803 and 2733 cm^{-1} was attributed to the aldehyde end groups of the p-TPTT polymer. These C-H peaks of the aldehyde groups also decreased. As a result, the FT-IR spectra have confirmed the structure of the synthesized p-TPTT copolymer.[10]

^{1}H NMR spectroscopy

The ^{1}H NMR spectrum of the p-TPTT copolymer was measured in DMSO-d_6 and the obtained result is demonstrated in Fig. 5. The p-TPTT polymer showed two different types of proton signals between 5 and 10 ppm. The aldehyde proton was observed at about 9.8 ppm and the aromatic protons of benzene were appeared as multiplets between 6.5 and 8.5 ppm. These results are agreed with the chemical structure of the p-TPTT copolymer.

SEM and optic microscopy of p-TPTT

The SEM and optic microscopy analyses of the prepared powder and the thin films of the p-TPTT polymer on ITO coated conductive glass substrate are demonstrated in Fig. 6. The microstructure images of the polymer powder shows large microparticles (50-300 μm) and some small spherical particles (1-20 μm) supporting the polymeric nature of the sample (Fig. 6a and b). Also, the surface morphology of the p-TPTT polymer is smooth and it agrees with its amorphous structure. The thin film on ITO substrate was prepared by the solvent casting method using the polymer solution in $CHCl_3$. The surface morphology of the thin film was examined by SEM and optic microscopy and the results were demonstrated in Fig. 6c-d and Fig. 6e-f respectively. Using the $CHCl_3$ as the solvent, the microstructure of the prepared film exhibited a good quality smooth surface and the homogenous morphology. The formation of grain boundary lines on the surface was also observed in some parts of the coating, but they can be avoided by controlling the deposition conditions and the film thickness. These results showed that the p-TPTT polymer dye has good film deposition properties for many practical applications.

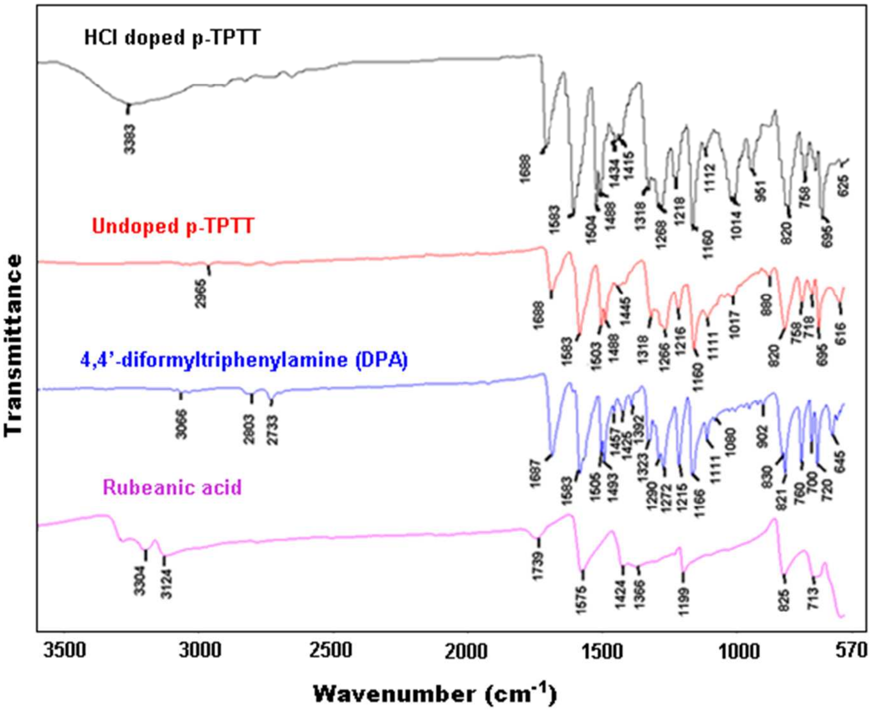

Fig. 4. FTIR spectra of rubeanic acid, DPA, HCl doped and undoped p-TPTT.

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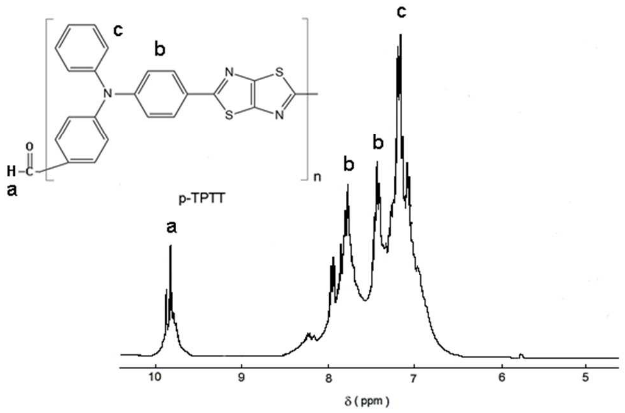


Fig. 5. ^{1}H NMR spectrum of p-TPTT polymer.

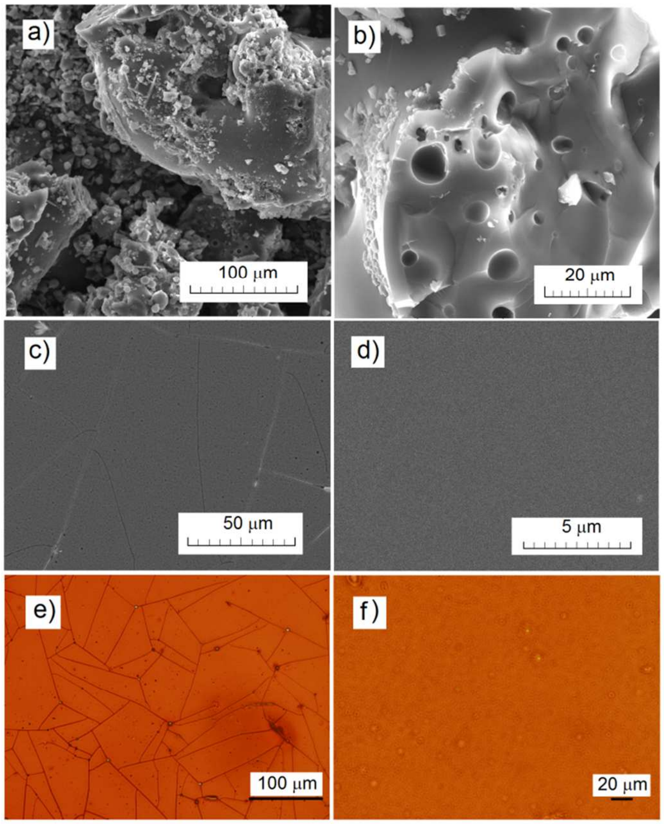


Fig. 6. SEM micrographs of p-TPTT polymer powder (a-b) and its thin film on ITO (c-d). Optical microscopy images of the polymer thin film (e-f).

Thermal analysis of p-TPTT

The thermal stability of the polymers is an important parameter for many applications such as solar cells and dye materials. To examine the thermal stability of the p-TPTT copolymer, the thermal analysis (TA) was performed from 25 to 750 °C temperature. The obtained TG and DTA curves from the TA measurements are given in Fig. 7.

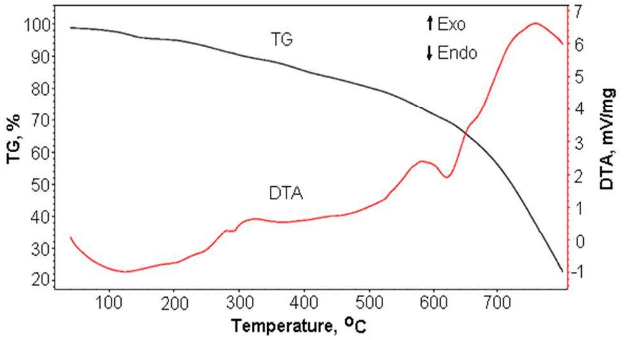


Fig. 7. Thermal analysis of p-TPTT polymer.

According to the TA results, the p-TPTT polymer showed a very good thermal stability up to 400-500 °C temperatures in air atmosphere. It means that the p-TPTT is highly air-stable polymer. The polymer burned and decomposed rapidly above 600 °C temperature. In addition, it was seen that the DTA curve of the polymer has exothermic peaks at the 280, 320, 580 and 760 °C temperatures. The peak at 760 °C can be attributed to the combustion of the polymer considering the DTA curve together with the TG. As a result, the p-TPTT polymer shows high thermal stability and it can be utilized for different applications.

UV-*vis.* absorption spectroscopy

The synthesized p-TPTT copolymer has been examined by UV-*vis.* spectroscopy. Firstly the UV-*vis.* spectra of the DPA monomer and p-TPTT copolymer were measured and compared with each other in Fig. 8. It was found that the p-TPTT copolymer has a maximum absorption at around 430-446 nm in CH_3CN and DMSO solvents while the DPA monomer has a maximum absorption band at 375 nm. These adsorption bands of p-TPTT at about 440 nm have been attributed to the thiazolo[5,4-*d*]thiazole group. The prepared copolymer structure contains two different chromophore groups and as expected, the uv-vis spectrum reflects the both absorption bands. The maximum absorption bands of polymer at 374 nm and 444 nm is assigned to the transitions of n- σ * of triphenylamine (C-N:) and the n- π* of thiazolo[5,4-*d*]thiazole (C=N:) groups respectively. This assignment is agree with the observed absorption band of DPA molecule at 375 nm and the band of phenylene thiazlo-thiazole molecule at 420 nm.[10] Furthermore, the optical absorption spectra of the p-TPTT polymer solutions in different solvents (DMSO, THF, $CHCl_3$, CH_3CN, toluene and acetone) were measured by using UV-*vis.* spectrophotometer. The obtained results are given in Fig. 9. The p-TPTT polymer showed similar absorption bands at around 376 and 446 nm wavelengths. The polymer solutions in various solvents resulted in the different absorption bands at around 244 nm. In addition, the molar absorptivity coefficients (ε, L/mol.cm) of the p-TPTT solutions were calculated by using the molecular weight of the repeating monomer unit. These results are given in Table 1.

The high molar absorptivity coefficients were found in $CHCl_3$, THF and DMSO, and the median absorptivity coefficients were observed in acetone and toluene. The lowest absorptivity coefficient was noted in CH_3CN. These results may be attributed to the strong polarity and the hydrogen bonding capability of DMSO, $CHCl_3$ and THF with the protons.

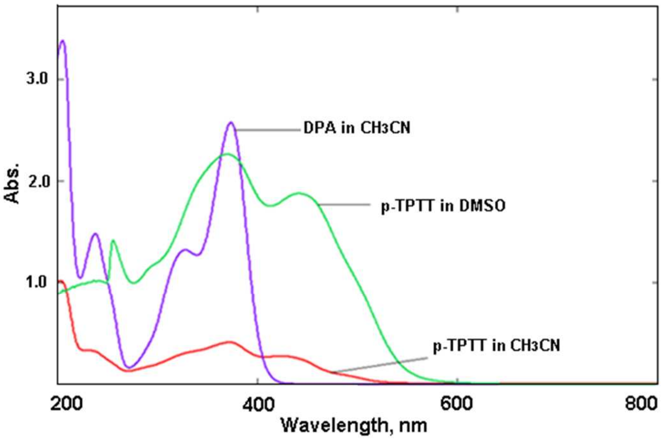


Fig. 8. UV-*vis.* spectra of DPA monomer and p-TPTT polymer.

Table 1.UV-*vis*. absorption and optical band gap energy values of p-TPTT in different solvents.

Solvent	λ_{max} (nm)	ε (L/mol.cm)	E_g^{Opt}	Solvent	λ_{max} (nm)	ε (L/mol.cm)	E_g^{Opt}
DMSO	259	173786		**CH_3CN**	204	49311	
	370	210650			374	19150	
	444	177138	2.79		430	13405	2.88
	555*	8139*	2.23*		530*	4788*	2.34*
THF	243	140178		**Acetone**	308	78994	
	366	179244			366	114900	
	443	165839	2.80		432	100538	2,87
	549*	4826*	2.26*		535*	5123*	2.32*
$CHCl_3$	244	147838		**Toluene**			
	376	180010			366	112985	
	446	159711	2.78		445	102261	2.79
	552*	6205*	2.25*		542*	4213*	2.29*

*: Obtained from the onset values of absorption bands.

The observed different absorption peaks in different solvents are due to changes in the intermolecular forces between the polymer chains. The polymer is highly soluble in $CHCl_3$, THF and DMSO and it exhibits higher absorptivity coefficients in these solvents. On the other hand, in toluene and acetone, the absorptivity is lowered since the probable formation of dimeric structures in solution and the lower solubility of the polymer. The polymer has significantly low absorptivity in CH_3CN because of the probable formation of larger aggregates by the hydrogen bonds and the other attraction forces.

In our previous work, we reported the spectroscopy of poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) copolymer. The chemical structures of poly(phenylene-thiazolo[5,4-*d*]thiazole) (p-PhTT) and poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) copolymers are given in Fig. 10. These polymers have very similar molecular structures. In this study, we have also compared the UV-*vis.* spectra of the p-PhTT and the p-TPTT copolymers in Fig. 11. The UV-*vis.* measurements were also taken after the NaOH addition to examine the further unprotonation of the copolymers.

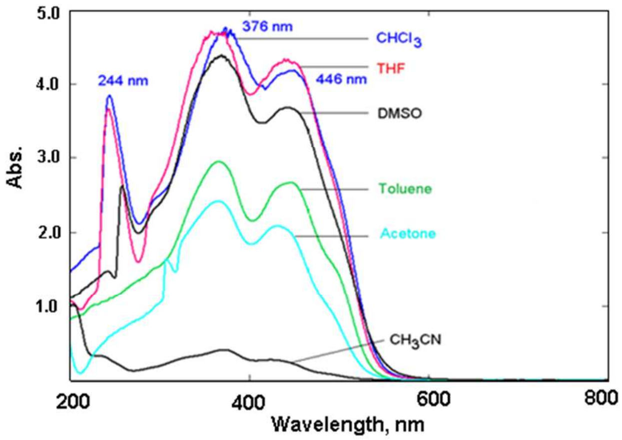
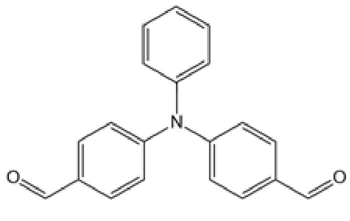
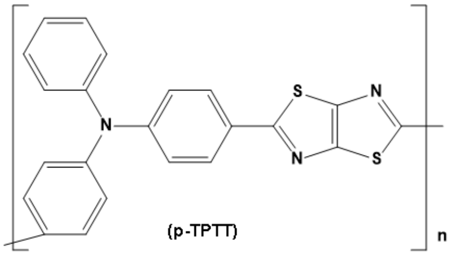
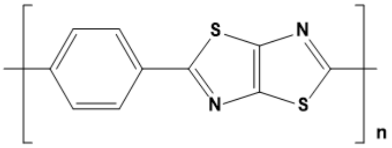


Fig. 9. UV-*vis*. spectra of p-TPTT polymer in different solvents.

In general, the spectra of the TPA copolymer (p-TPTT) red shifted to the lower energy wavelengths compared to the spectra of the phenylene copolymer (p-PhTT). For the both polymers, NaOH addition also resulted in red shifted absorption bands. In addition, the optical band gap energies (E_g^{Opt}) of the p-PhTT and p-TPTT copolymers were calculated from their absorption edges (λ_{onset}) and maximums (λ_{max}) according to the Planck's equation ($E_g = 1240/\lambda$).[1,36] The obtained E_g^{Opt} values are given in Table 2. The optical band gap values of 2.23 and 2.79 eV were found from the onset and the maximum absorption bands of the p-TPTT polymer, respectively. Very little changes in the band gap energies were seen according to the solvent type. It was noted that NaOH addition to the p-TPTT polymer solution in DMSO resulted in further unprotonated (undoped) polymer. The NaOH addition lowered the optical band gap values from 2.23 to 1.85 eV for the onset and from 2.79 to 2.28 eV for the maximum. The E_g^{Opt} values of the DPA as precursor material for the p-TPTT were also calculated as 3.31 eV from the maximum and 2.95 eV from the onset. In our previous work, the E_g^{Opt} values of the phenylene-polymer (p-PhTT) were calculated as 2.14 from the onset and 2.56 eV from the maximum.[11] These results showed that the optical band gap energy decreased significantly with the presence of TPA unit in the polymer chain.

In addition, the solid phase UV-*vis.* spectra of the powder and the thin film coating of the p-TPTT polymer were measured. The obtained powder and thin film UV-*vis.* spectra of the p-TPTT polymer are given in Fig. 12. The observed new absorption band at about 680 nm in the UV-*vis*. spectrum of the polymer thin film can be attributed to the charge transfer band. The results were compared with each other in Fig. 12. According to the UV-*vis.* spectra of the powder samples, the p-TPTT polymer showed the absorption bands up to 800 nm wavelength corresponding to 1.55 eV. This shows that the p-TPTT polymer has low band gap energy (E_g^{Opt}=1.55 eV). On the other hand, the p-PhTT powder, a phenylene-thiazolo type polymer, has an absorption band below 650 nm corresponding to 1.91 eV. Based on the UV-*vis.* spectroscopic studies, it was concluded that the p-TPTT polymer with low E_g^{Opt} energy is a suitable polymer material for the solar cells.

Table 2. UV-*vis.* absorption and optical band gap energy values of DPA, p-TPTT and p-PhTT.

Sample	Solvent	λ (nm)	E_g^{Opt}
 4,4'-diformyltriphenylamine (DPA)	CH_3CN	375 420*	3.31 2.95*
	DMSO	444 555*	2.79 2.23*
	DMSO + NaOH	545 670*	2.28 1.85*
 (p-PhTT)	DMSO	264 490*	4.70 2.53*
	DMSO + NaOH	485 580*	2.56 2.14*

*: Obtained from the onset values of absorption bands.

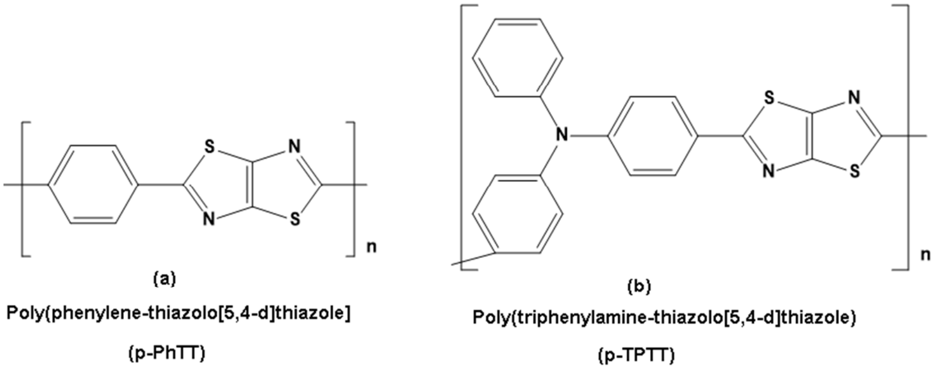


Fig. 10. Poly(phenylenethiazolo[5,4-*d*]thiazole) (p-PhTT) (a) and poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) (b) copolymers.

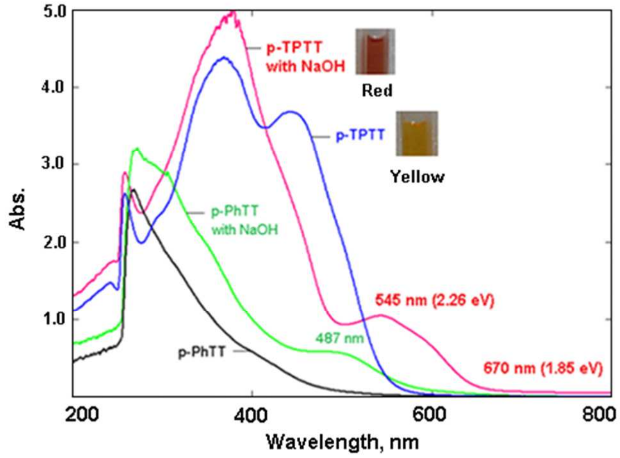


Fig. 11. UV-*vis*. spectra of poly(phenylenethiazolo[5,4-*d*]thiazole) (p-PhTT) and poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) copolymers.

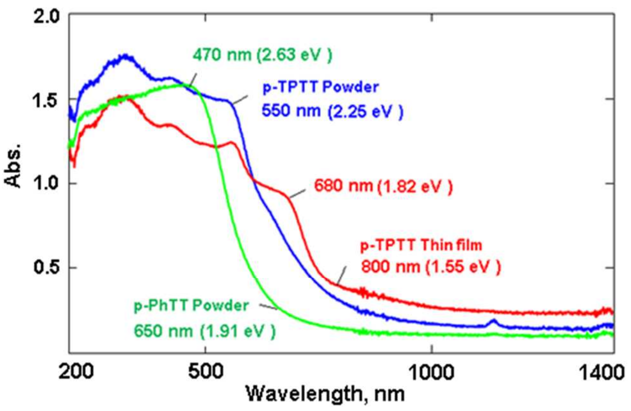


Fig. 12. UV-*vis*. spectra of poly(phenylenethiazolo[5,4-*d*]thiazole) (p-PhTT) and poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT).

Fluorescence spectroscopy

The fluorescence (FL) spectroscopy was used for the characterization of the synthesized p-TPTT polymer. The FL spectra of the p-TPTT polymer solutions in CH_3CN, DMSO, toluene, $CHCl_3$ and THF solvents were measured. The all polymer solutions in these solvents showed FL emissions. The FL emission colors were observed as green in toluene and THF, yellow-green in $CHCl_3$ and DMSO, and blue-green in CH_3CN under a UV lamp. Among these solvents, the detailed FL spectra of the polymer solutions in CH_3CN and DMSO are measured on a spectrofluorimeter and the results are given in Fig. 13. When the p-TPTT solution in CH_3CN was excited at both 374 and 430 nm, it gave a FL emission at 500 nm. It was seen that the FL emission in the CH_3CN solvent increased with the excitation at 430 nm. If the results of FL experiments in DMSO are examined, the FL emissions at 520 and 522 nm were seen using 370 and 444 nm excitations, respectively. The Stokes shifts of the FL emissions of the p-TPTT polymer were calculated as 73 and 126 nm for the CH_3CN solution and as 78 and 150 nm for the DMSO solution.

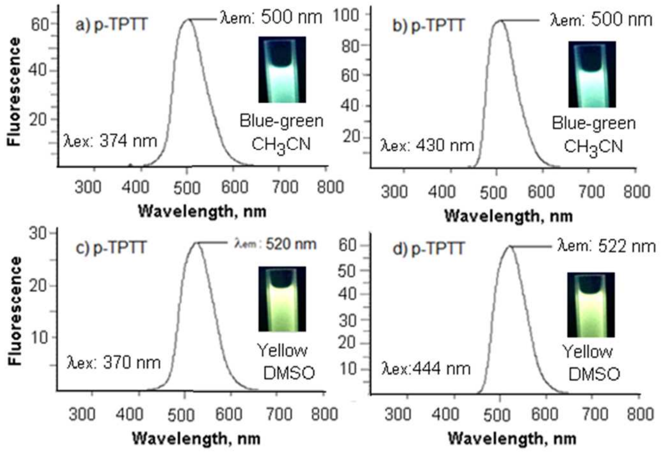


Fig. 13. Fluorescence spectra of p-TPTT polymer solutions in CH_3CN (2 mg/100 mL) and DMSO (12 mg/100 mL).

Furthermore, the FL spectroscopic analysis of the p-TPTT polymer were compared with the DPA monomer and the phenylene-thiazolo type polymer (p-PhTT) which was reported previously.[11,12] The FL spectra of DPA and phenylene-thiazolo polymer (p-PhTT) are given in Fig. 14. The DPA is a fluorescent material and it emits fluorescent light at 493 nm with 374 nm excitation. The phenylene-thiazolo[5,4-*d*]thiazole (p-PhTT) polymer has a FL emission at 459 nm with 370 nm excitation. The triphenylamine-thiazolo[5,4-*d*]thiazole polymer (p-TPTT) shows FL emissions at 500 and 522 nm. The FL measurements shows that poly(triphenylamine-thiazolo[5,4-*d*]thiazole) could be used a fluorescent polymeric dye material.

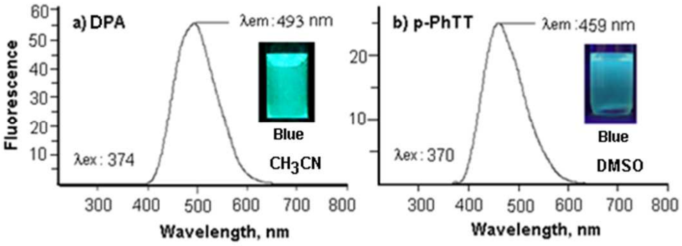


Fig. 14. Fluorescence spectra of a) DPA and b) p-PhTT polymer.

Cyclic voltammetry

The electrochemical properties of the synthesized p-TPTT copolymer and DPA molecule were examined by using the cyclic voltammetry (CV). The obtained voltammograms of the DPA and p-TPTT copolymer are given in Fig. 15. It was determined that DPA molecule has the anodic and cathodic potentials at 1.20 and -0.60 V, respectively. The synthesized p-TPTT polymer showed the anodic and cathodic peaks at 1.35 and -0.61 V potentials. The $E_{1/2}$ values of these anodic and cathodic peaks were used in the calculation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels.[10-12,37]

HOMO, LUMO and band gap energies

The HOMO, LUMO and the band gap energy levels of polymers are very important in solar cell systems and electro active materials. In this study, especially we focused on the band gap energy of the synthesized p-TPTT copolymer. Firstly, the HOMO and LUMO levels were calculated from the anodic ($E_{1/2}^{Ox}$) and cathodic ($E_{1/2}^{Red}$) peak potentials in the CV voltammograms by using the Eqs. 1 and 2. Then, the electrochemical band gap energy (E_g^{CV}) of the p-TPTT polymer was obtained from the difference of the HOMO and LUMO values by using Eq. 3.[11,12,37,38] The calculated HOMO, LUMO and the E_g^{CV} energies are given in Table 3 and compared with the E_g^{Opt} energy values.

HOMO : - ($E_{1/2}^{Ox}$ + 4.34) eV (1)
LUMO : - ($E_{1/2}^{Red}$ + 4.34) eV (2)
E_g^{CV} : - (HOMO - LUMO) eV (3)

A favourable polymeric material for good efficiency in organic solar cells requires the critical HOMO and LUMO energy levels. The oxidation threshold of air is about -5.3 eV against vacuum level.[38] Therefore, the HOMO level cannot be more positive than this value to provide the air stability of the polymer. The ideal LUMO level for polymers should be in the range of -3.7 and -4.0 eV to transfer the electrons from the polymer to the acceptor layer between ITO and Al.[38] As a result of these specific HOMO and LUMO levels, the band gap energy of an ideal polymeric material for the organic solar cells should be below 2.0 eV.[38] The p-TPTT polymer is a very suitable polymer for the organic solar cells, considering its HOMO (-5.32 eV), LUMO (-3.96 eV), $E_g^{Opt.}$ (1.55 eV) and E_g^{CV} (1.36 eV) energy levels.

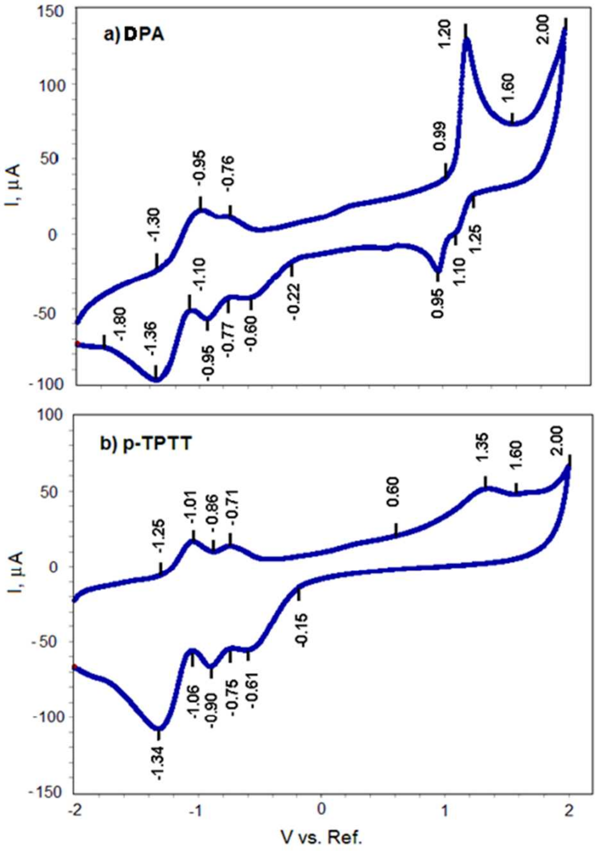


Fig. 15. Cyclic voltammograms of DPA and p-TPTT.

In addition, some literature results about the band gap energies of TPA or thiazolo[5,4-d]thiazole containing polymers are also given in Table 4. As a result, the prepared p-TPTT polymer has a relatively low band gap energy compared to the literature values of the other TPA and thiazolo[5,4-d]thiazole polymers (Table 4).

Table 3. HOMO, LUMO and band gap energies of p-TPTT and p-PhTT copolymers

Sample	UV-*vis*. optical absorption			
	λ_{Max} (nm)	$E_g^{Opt, Max}$ (eV)	λ_{Onset} (nm)	$E_g^{Opt, Onset}$ (eV)
p-PhTT powder	470	2.63	650	1.91
p-TPTT powder	680	1.82	800	1.55
p-TPTT Film	550	2.25	800	1.55
	Electrochemical CV			
	HOMO (eV)	LUMO (eV)	E_g^{CV} (eV)	
p-TPTT in CH_3CN	-5.32	-3.96	1.36	

Table 4. Band gap energies of some TPA or thiazolo[5,4-*d*)thiazole containing polymers.

Groups in polymeric backbone	Band gap (eV)
Sulfonatobutyloxytriphenylamine-phenylene[29]	2.87 - 2.99
Sulfonatotriphenylamine-phenylene	
Cyanoacetic acid-triphenylamine-thiophene[9]	2.15
Polythiophene containing triphenylamine moity[39]	2.03 - 2.54
Triphenylamine- and oxadiazole-substituted poly(1,4-phenylenevinylene)s[40]	1.83 – 2.40
4-Metoxy-triphenylamine[8]	2.83
Triphenylamine-ditihopene[41]	1.93
Furyl- thiazolo[5,4-*d*]thiazole[42]	2.00
Thiophene-thiazolo[5,4-*d*]thiazole[18]	1.80
Decylthiophene-thiazolo[5,4-*d*]thiazole-didecyloxynaphthalene[19]	2.21
2,5-Dithienyl-thiazolo[5,4-*d*]thiazole[22]	1.79
Bithiazole-thiazolo[5,4-*d*]thiazole	1.82-1.99
Benzodithiophene-thiazolo[5,4-*d*]thiazole	
Didecylfluorene-hexylthiophene-thiazolo[5,4-*d*]thiazole	1.80-2.14
Dioctyldibenzosilole-hexylthiophene-thiazolo[5,4-*d*]thiazole][23]	
Thieno[3,2-b]thiophene-thiazolo[5,4-*d*]thiazole[43]	1.82-1.85
Triazol-thiophene-thiophene-thiazolo[5,4-*d*]thiazole[44]	1.7-1.9
Triazol-furan-thiazolo[5,4-*d*]thiazole	
Dioctyloxybenzo-dithiophene-thiazolo[5,4-*d*]thiazole[45-47]	1.68-2.34
Dithieno-silole-thiazolo[5,4-*d*]thiazole[30]	1.73-1.77
Triphenylamine-azomethine[48]	2.41

Experimental Section

Materials

4,4'-diformyltriphenylamine (Bis(4-formylphenyl)phenylamine) was obtained from Sigma–Aldrich (Chemie GmbH, Taufkirchen, Germany). Rubeanic acid (Dithiooxamide) was purchased from Fluka (Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany). They were used in the synthesis of poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) copolymer as received. Dimethylsulfoxide (DMSO), acetonitrile (CH_3CN) and and the other solvents were obtained from Merck (Darmstadt, Germany). Lithium perchlorate ($LiClO_4$) was from Fluka (Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany). The other chemical reagents were analytical grade.

Synthesis of p-TPTT copolymer

In this study, a new poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) alternating copolymer (systematically named as poly(*N*,*N*-diphenylphenylamine-4′,4′′-diyl-co-thiazolo[5,4-*d*]thiazole)) was synthesized from the reaction of 4,4'-diformyltriphenylamine (bis(4-formylphenyl)phenylamine) (DPA) and rubeanic acid (dithiooxamide) by using a similar method (Fig. 2). For the synthesis of the p-TPTT copolymer, 1.20 g (4 mmol) 4,4'-diformyl-triphenylamine and 0.48 g (4 mmol) rubeanic acid were mixed in 50 mL ethanol and started to heating up to 80 °C under stirring conditions. Then, 2 mL 0.5 M NaOH solution was added into the solution. A dark brown copolymer precipitated after heating for 24 h at 80 °C. The obtained polymer was filtered and washed several times with acetone and then dried at 105 °C. The obtained polymer was 0.27 g and it was labelled as an undoped p-TPTT copolymer. As demonstrated in Fig. 2, the HCl doped form of the copolymer was obtained in acetone by adding 0.5 M HCl solution. The HCl doped polymer was also washed and dried at 105 °C.

Experimental measurements and characterization of p-TPTT

The molecular weight of the synthesized p-TPTT copolymer was determined by using a gel permeation chromatography (GPC, Shimadzu) instrument. Polystyrene standards were used for the calibration of the GPC instrument. The measurements were performed using the polymer solution in THF. The Mn and Mw values of the p-TPTT were found for the different fractions. The FT-IR spectra of the HCl doped and undoped p-TPTT polymer samples, and the initial monomers were recorded on a Perkin Elmer Spectrum Two model spectrophotometer. The powders of the samples were used in the FT-IR measurements. The ^1H NMR spectra of the p-TPTT polymer was performed on a 300 MHz NMR spectrometer (Varian Mercury Plus) in DMSO-d_6. The SEM microscopic analyses of the p-TPTT powder and the thin film were recorded by using a TESCAN VEGA3 instrument. The optical micrographs of the thin film were obtained by Olympus microscope. The thermogravimetric analyses (TG and DTA) of the p-TPTT were carried out by using NETZSCH STA 449F1 model thermal analyzer. About 50 mg of the polymer sample was filled into alumina crucible, and then the measurements were carried out from 25 to 750 °C with a heating rate of 10 °C/min under air atmospheric condition.

The UV-*vis*. spectra of the HCl doped and undoped p-TPTT polymer solutions were recorded on a Shimadzu UV-*vis*. 2600 PC model double beam spectrophotometer between 200 and 800 nm. For the UV-*vis*. measurements, the polymer solutions were prepared in DMSO, THF, $CHCl_3$, CH_3CN, toluene and acetone at 8-10 mg/100 mL concentrations. The UV-vis. measurements in DMSO were obtained after adding NaOH solution for the deprotonation of the polymer. Furthermore, the UV-*vis.* absorption spectra of the p-TPTT powder and the thin film were also measured between 200 and 1400 nm by using ISR attachment.

The fluorescence (FL) emission colors of the p-TPTT solutions in DMSO, THF, CHCl$_3$, CH$_3$CN, toluene and acetone were determined by using a UV-lamp. The fluorescence (FL) spectra of the p-TPTT polymer and the TPA monomer in DMSO and CH$_3$CN were taken by using Hithachi F-2710 model spectrofluorimeter. For this purpose, the p-TPTT solutions in DMSO and CH$_3$CN were prepared at 2-8 mg/100 mL concentrations. The FL measurements of p-PhTT polymer were performed by exciting at the different wavelengths (370, 374, 430 and 444 nm) corresponding to the maximum absorption values.

The cyclic voltammetric measurements of the p-TPTT polymer and TPA monomer were performed on a Gamry 750 EQCM model potentiostat at the scanning rate of 100 mV/s between -2.0 and 2.0 volt. The measurements were carried out by using Ag/AgCl reference electrode (E= +0.197 V) and two platinum electrodes as the working and the counter electrodes. In the measurements, LiClO$_4$ was used to provide the electrolytic conductivity of the p-TPTT and TPA solutions in CH$_3$CN.

Conclusions

In this work, poly(triphenylamine-thiazolo[5,4-*d*]thiazole) (p-TPTT) copolymer, a new low-band gap and fluorescent dye material, was synthesized. The p-TPTT copolymer was examined by using UV-*vis.* absorption, fluorescence, FT-IR and ^{1}H NMR spectroscopy, cyclic voltammetry and thermal analysis. It was observed that the p-TPTT is a soluble polymer in commonly used organic solvents, such as DMSO, CH$_3$CN, acetone, toluene, CHCl$_3$ and THF. The thermal analysis showed that the p-TPTT is highly air-stable polymer up to 400-500 °C temperatures. From the CV measurements, the HOMO and LUMO energy levels of the copolymer were found as -5.32 and -3.96 eV, and electrochemical (E_g^{CV}) band gap energy was obtained as 1.36 eV. The optical ($E_g^{Opt.}$) band gap energies were calculated as 1.85 eV in DMSO and 1.55 eV in the form of solid powder based on the UV-*vis*. measurements. Also, the p-TPTT polymer exhibited strong FL emissions at 500 and 522 nm wavelengths. It was concluded that the p-TPTT copolymer with the optimal HOMO, LUMO and the band gap energies is a very good candidate material for the technological applications. Also, it can be utilized as a fluorescent dye in electrooptic OLED and organic photovoltaic (OPV) applications considering its low band gap energy, high thermal stability and solubility properties.

Notes

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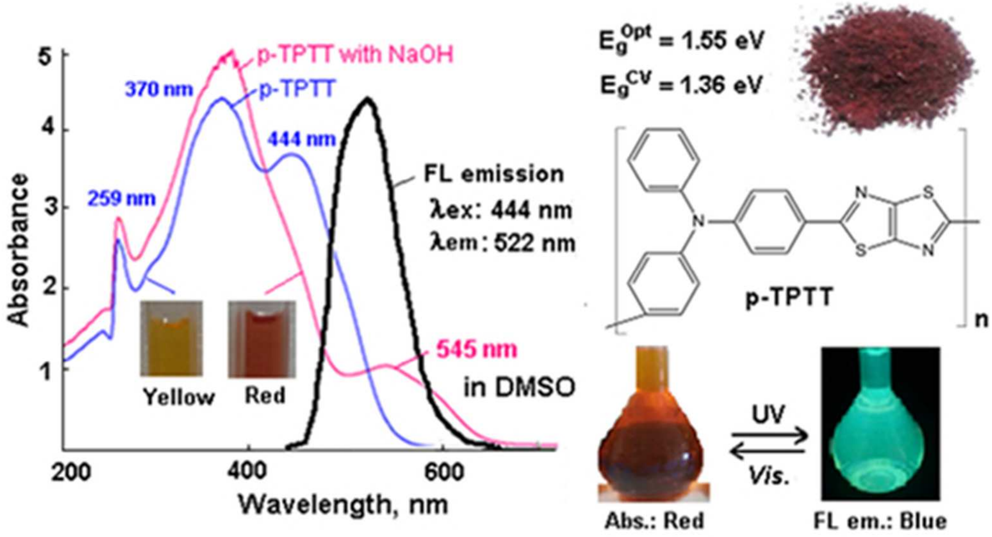

The synthesis, characterization and spectroscopy of a new fluorescent poly(triphenylamine-thiazolo[5,4-d]thiazole) dye with low band gap energy have been reported.
48x26mm (300 x 300 DPI)