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Chemical Changes and Photoluminescence Properties of UV Modified Polypyrrole

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Effects of ultraviolet light (325 nm) irradiation on polypyrrole (PPy) properties were studied by time-resolved, standard photoluminescence (PL), optical absorption, and X-ray photoelectron (XPS) spectroscopies. PPy samples were prepared in thin films on gold, quartz, and H-terminated monocrystalline diamond (MCD) substrates by electrochemical and chemical oxidation. After the UV irradiation, all PPy samples converged to the same PL spectrum independent of initial preparation methods or substrates. We observed formation of a new, highly intensive PL band at 540 nm accompanied with few per cent increase in transmittance and structural and chemical changes of the PPy chains. The changes occurred only when the light intensity was from 0.1 to 10 W/cm^2. The effect was reduced in vacuum. Thermal annealing had no influence. We explain the effect by chemical and structural modifications of PPy that lead to a permanent increase in quantum yield of intrachain exciton recombination.

Keywords: Polypyrrole; Photoluminescence; UV light modification; Time-resolved PL

1. INTRODUCTION

Polypyrrole (PPy) is an organic dye and one of the most investigated conductive polymers. Although PPy has been known for nearly a century, it received great attention after the breakthrough of conductive polymers in the beginning of 80's [1]. Its main advantages are high electrical conductivity, biocompatibility, pH sensitivity, good stability in ambient conditions, and rather easy preparation [2-5]. During the years the main synthesis methods - polymerization by chemical or electrochemical oxidation - have been extended by many others such as matrix assisted pulsed laser evaporation or chemical vapor deposition [6-8]. PPy properties are widely adjustable by the variation of preparation conditions [2, 9]. Strong interchain interaction that limits solubility of the polymer can be reduced by chemical attachment of functional group on pyrrole ring [10] or by doping by anionic surfactant [11]. In addition to the original use as a dye, PPy is involved in many advanced applications in electronics, optoelectronics [12,13], photovoltaic [14] and biomedicine [15, 16] nowadays.

PPy belongs to the group of conductive polymers with non-degenerate ground state that significantly influence its optical and electrical properties [17]. The main charge carriers in these polymers are polarons and, after sufficient amount of doping, bipolarons instead of solitons [9, 18]. Band gap size depends on conditions of synthesis and the typical value of pristine PPy is about 390 nm (3.2 eV) [19]. PPy also shows high sub-band gap absorption that is explained by transitions between valence band (HOMO), polaron, and bipolaron states [20]. In spite of the intense broad-band absorption and in contrast to other polymers with non-degenerate ground state, PPy shows only very low photoluminescence (PL) quantum yield [21]. Intensive PL is exclusively observed only on PPy nanoparticles and PPy dispersed in specific organic solvents [15, 22]. In these articles PPy shoved broad PL band with the maximum between 450 nm - 530 nm and the interpretation of its origin is still controversial.

One of the most fundamental drawbacks of conductive polymers is their vulnerability to ultraviolet (UV) light [23-25]. Light induced modifications have a major impact on function of photovoltaic and optoelectronic devices. On the other hand, once sufficiently understood, these modifications could become a useful tool for intentional after-preparation alteration of conductive polymers properties and increase the application range of conductive polymers [26, 27]. However, this issue is still weakly understood and existing publications mostly concentrate on highly luminescent polymers such as poly(p-phenylene vinylene) (PPV) or polythiophene (PT) [28-30].

We address this issue and present a study of UV-induced modifications of PPy. We focus on elucidating the origin of observed changes and on development of methodology for their monitoring. For this purpose we use time-resolved and standard photoluminescence spectroscopy as a tool sensitive to material properties and defects, and XPS for detection of elemental and structural changes. These methods have been already successfully used to characterize photophysical properties of highly luminescent conjugated polymers [30], but yet not been applied to organic dyes such as PPy.

2. EXPERIMENTAL PART

2.1 Polypyrrole synthesis

PPy was electrochemically synthesized from solution of pyrrole (240 mM; Aldrich) and NaCl (100 mM) in deionised water. The electrochemical deposition was performed in area of 2 mm^2 in galvanostatic regime, applying the current from 500 nA to 10 μA for 120 to 300 s by a potentiostat

(Autolab PGSTAT302) between the substrate and the counter electrode (Pt) [32]. Size of the used droplet was 0.3 μl. Gold and surface conductive H-MCD we used as the substrates [12]. These materials were chosen to characterize influence of the substrate electronic properties and PPy bonding to the substrate on the UV modifications and PPy properties in general. The choice of H-MCD was also motivated by a wide range of foreseen applications of diamond-polymer structures. After the synthesis, the PPy layers were rinsed by deionised water and dried by compressed air. Thickness of the prepared layers was dependent on deposition current, time, and conductivity of the employed substrate and varied from 10 to 100 of nm as determined by atomic force microscopy (AFM).

Chemically prepared PPy was synthesized by chemical oxidation from the solution of Pyrrole (240 mM; Aldrich) and HCl (0.8 mM) in deionised water. After polymerization, 2 μl of PPy solution was drop-casted in the area of 4 mm^2 on a spectrally pure quartz glass (Suprasil) or H-MCD surface. Thickness of these layers was dependent on size and volume of the drop and varies from 10 to 100 of μm as determined by profilometer.

2.2 Optical characterization

The standard PL spectra were measured by the grating spectrograph with CCD camera (Andor DV420A) and were corrected for the spectral sensitivity of the whole setup. The lines at 325 nm (3.82 eV) and 442 nm (2.81 eV) of a continuous wave He-Cd laser (Omnichrome T2056-MA03, Melles Griot) were used for the PPy sample irradiation. Only the UV line was used for PL excitation.

For the time-resolved PL measurements the Ti-sapphire femtosecond laser (Tsunami 3960, Spectra-Physics with the regenerative amplifier Spitfire PRO-F1KXP (Spectra-Physics) was used. The parameters of femtosecond pulses were: wavelength 400nm, repetition rate 1 kHz, pulse time length 100 fs and maximal pulse energy 0.01mJ. Time decay of the PL was measured by the streak camera C5680 (Hamamatsu) in the range from ns to ms.

For the low pressure measurements we used a cryostat chamber and a cascade of oil and turbomolecular pump. Thermal annealing of the samples was carried out on a commercial hotplate in the presence of air.

2.3 XPS characterization

XPS signals were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.6 eV). An X-ray beam of 100 μm size was used at 1.16 mA x 12 kV. The spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected using the snapshot acquisition mode (150 eV pass energy). The narrow region data was postprocessed using Jansson’s algorithm to remove the analyzer point spread function, resulting in improved resolution of the spectra for peak deconvolution. Charge compensation was achieved with the system flood gun that provides low energy electrons (~0 eV) and low energy argon ions (20 eV) from a singe source. The argon partial pressure was $2x10^{-7}$ mbar in the analysis chamber. The Thermo Scientific Avantage software, version 4.84 (Thermo Fisher Scientific), was used for digital acquisition and data processing.

Spectral calibration was determined by using the automated calibration routine and the internal Au, Ag and Cu standards supplied with the K-Alpha system.

The surface compositions (in atomic %) were determined by considering the integrated peak areas of detected atoms and the respective sensitivity factors. The fractional concentration of a particular element A was computed using:

$$\%A = \frac{I_A / s_A}{\sum (I_n / s_n)} \times 100\% , \qquad (1)$$

where In and sn are the integrated peak areas and the Scofield sensitivity factors corrected for the analyzer transmission, respectively.

3. RESULTS AND DISCUSSION

3.1. Optical characterization of PPy UV modification

Fig. 1 shows the time evolution of normalized PL spectra of electrochemically and chemically prepared PPy during UV irradiation (325 nm, 5W/cm^2) for up to 2 hours. The PPy was prepared on the H-MCD substrate. For electrochemical PPy the original PL spectrum is dominated by high-frequency broad band of low intensity. During UV irradiation a new broad band with the maximum around 540 nm (2.30 eV) appeared and increased by more than 1000% compared to the original PL intensity. Initial fast increase of the PL intensity saturated within 1 to 3 hours depending on the excitation intensity. The rate of the PL changes depended on excitation light intensity and was rising with increasing intensity in the interval from 0.1 W/cm^2 to 10 W/cm^2. Light intensity I $\leq$ 0.1 W/cm^2 did not induced detectable modification, however I $\geq$ 10 W/cm^2 caused burning of the polymer.

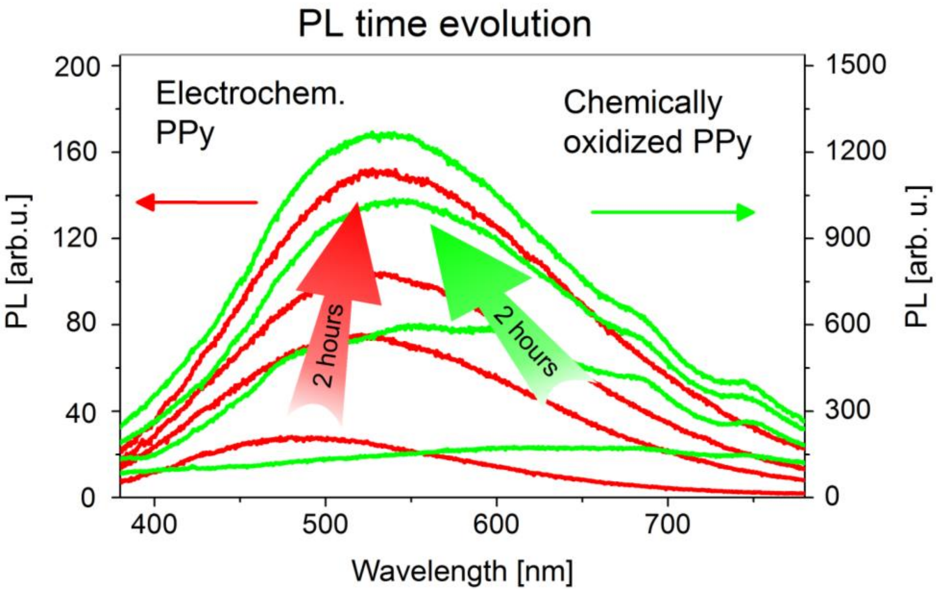

Figure 1. Time evolution of normalized PL spectra of PPy during UV irradiation (325 nm and 5W/cm^2 for up to 2 hours). Red curve - electrochemically prepared PPy on H-MCD, green curve - chemically prepared PPy on pure quartz glass. (Colour on-line)

Similar behavior was observed also for PPy prepared by chemical oxidation (see also Fig.1, green spectra) although its initial PL spectrum was different. In the end, there was only small mismatch (5 - 15 nm) in the position of PL maximum on samples prepared by various methods. In both cases, the photo-induced PL changes were permanent (ΔPL $\leq$ 1% at the band maximum after 4 hours) and independent of deposition conditions or used substrates.

Not only PL of PPy is being modified during UV light irradiation. Optical transmittance measurements in Fig. 2 reveal that also absorption of the PPy layer is being quenched. In the broad and strong transmittance spectra we could recognize a decrease at 420 nm that indicates the edge of interband absorption and corresponds to the PL spectrum of electrochemically synthesized PPy from the Fig. 1. The rest of the broad spectrum can be formed by various transitions as discussed further below.

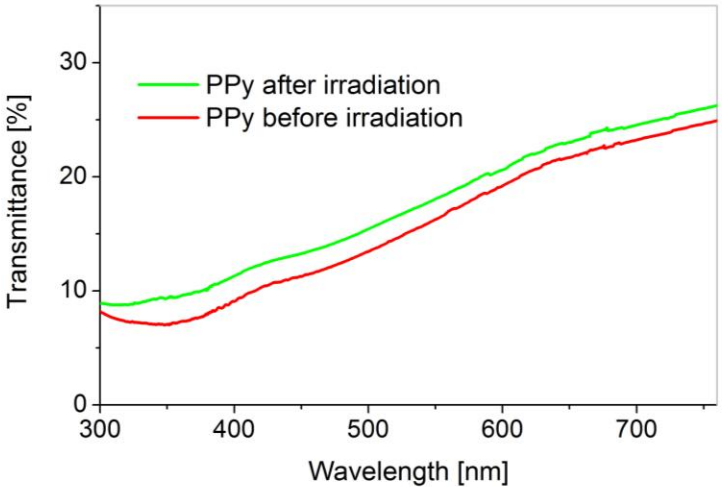

Figure 2. Transmittance of electrochemically synthesized PPy layer on H-MCD before and after UV irradiation (325 nm and 5W/cm^2 for 2 hours). (Colour on-line)

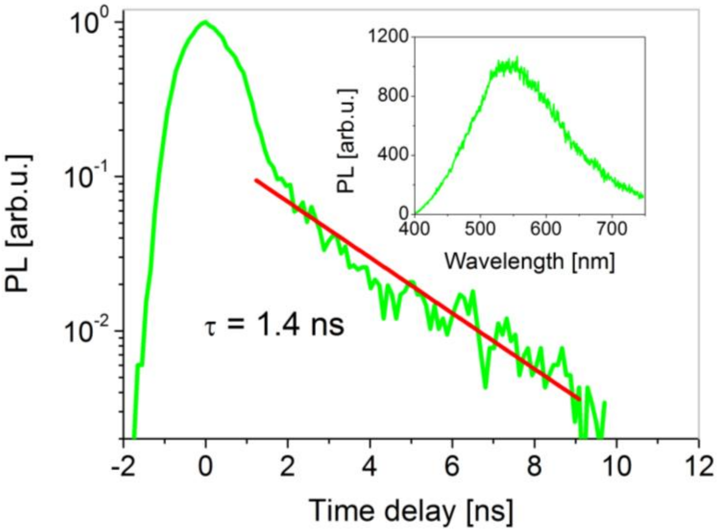

Figure 3. PL time decay of chemically prepared PPy on H-MCD. Parameters of the excitation: wavelength 400 nm, repetition frequency 1 kHz, pulse time length 100fs and maximal pulse energy 10 μJ. PL was measured at 540 nm. Time integrated PL spectrum is presented in inset. (Colour on-line)

To understand the processes behind the new PL band, measurement of time-resolved PL is fundamental. Fig. 3 shows time-resolved PL on UV-modified chemically prepared PPy on H-MCD. The decay of PL at 540 nm is composed of two components. The first one is much faster than the used streak-camera time resolution. The slower one showed mono-exponential decay with the time constant of 1.4 ns. The time-resolved PL of PPy was measured from 1 ns to 1 ms, but no detectable signal with longer time constant was observed. Unfortunately, the PL signal from the original PPy was too low to be detected by our setup, so we cannot compare the decay times of the original and modified samples.

3.2. Role of UV light and thermal energy

Possible influence of thermal energy in the observed modifications was characterized by PL measurements of thermally annealed PPy layers. The PPy layers were electrochemically deposited on the gold substrate. Annealing was carried out in the presence of air at temperatures 370, 420, 480 and 520 K. The PL excitation UV light intensity 100 mW/cm^2 was intentionally chosen below the photo-induction threshold so that only changes in PL spectrum due to the annealing are monitored. The results showed (Fig. 4) that no change in PL band from 400 to 600 nm occurred after annealing. On the other hand, some PL rise in the region ≥ 600 nm was detected after reaching the temperature of 470 K and continues at 520 K. Such kinds of changes are usually associated with carbonization (burning) of the organic material. Further increase of the temperature would be therefore pointless. These results exclude thermally initiated modification of the PPy chains as possible origins of the photo-induced PL enhancement.

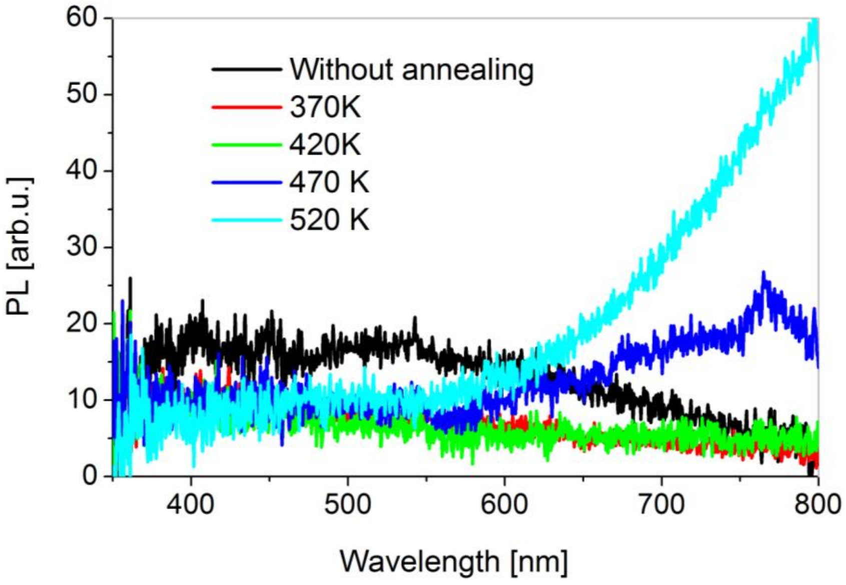

Figure 4. PL spectra of electrochemically prepared PPy on gold substrate that was annealed for 2 hours at various temperatures from 370 K to 520 K. (Colour on-line)

The essential role of the UV light in modification and change of PL characteristics of PPy was evidenced by comparing effects of irradiation at 325 and 442 nm. Two samples of PPy were prepared in the exactly same way by chemical oxidation and subsequently deposited on H-MCD substrates. The first sample was irradiated by UV light at 325 nm and intensity of 5 W/cm^2, the other one by light at

442 nm with intensity of 50 W/cm^2. In regular 10 min time intervals, the irradiation was interrupted and PL spectra of both samples were measured. The PL was excited at 325 nm and 100 mW/cm^2. Fig. 5 shows the evolution of PL intensity at 540 nm as function of exposure time for both samples. PL intensity of the layer irradiated by UV light increased 10 times before saturation. PL intensity of the second PPy sample irradiated by 442 nm only doubled its original value although the excitation intensity was 10 times higher. This result demonstrates not only clear necessity of UV excitation for efficient PPy modification, but also confirms our previous observations, which exclude the thermal origin of the PL enhancement.

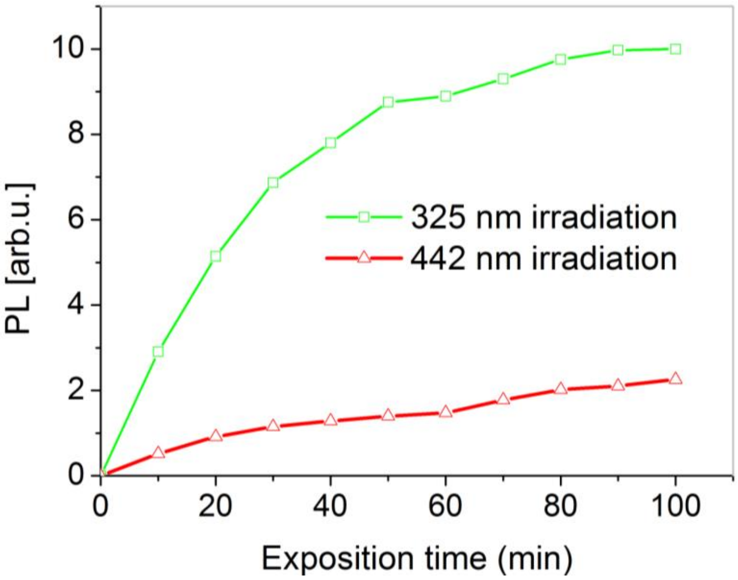

Figure 5. PL Intensity of chemically synthesized PPy layers irradiated by laser beam of 325 and 442 nm for 100 min. PL intensity was monitored at 540 nm. (Colour on-line)

3.3. Role of ambient conditions

UV photo-induced changes of polymers are commonly linked with creation oxygen containing functional groups like aldehydes and ketons [33]. Therefore, the influence of ambient condition on UV modifications has been carried out in order to elucidate background of the observed phenomenon. The electrochemically prepared PPy on gold substrate was placed into the cryostat chamber that was evacuated to the pressure about 0.01 Pa. PL spectra during UV irradiation were measured and compared to the same measurement in air. The results in Fig. 6 show that not only UV light but also presence of air is needed for the PPy modification. Under the atmospheric air pressure there was an up to order of magnitude increase in PL intensity at around 540 nm (PL band maximum). On the other hand, just 3x increase of PL intensity was detected at 540 nm after the modification in vacuum. Small PL side band of PPy with the maximum around 400 nm is attributed to the direct interband transition.

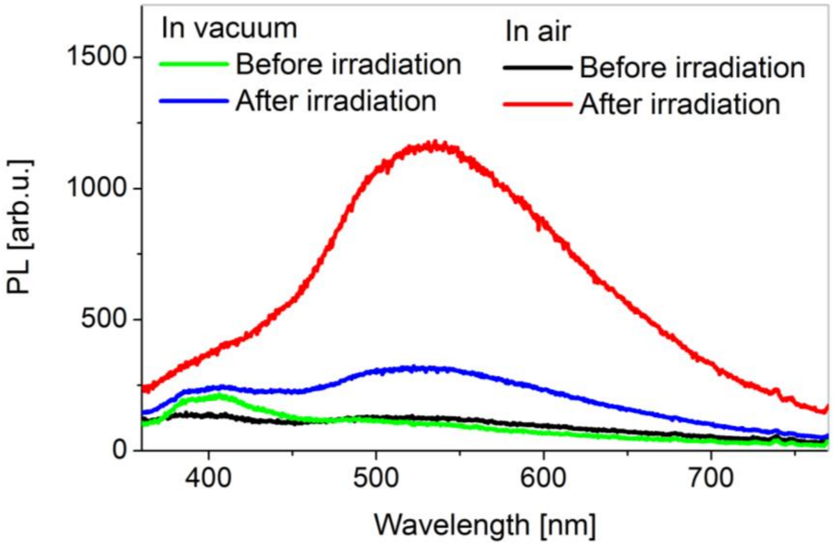

Figure 6. Comparison of PL changes of electrochemically prepared PPy on gold substrate after three hours of UV irradiation (325 nm, 5 W/cm^2) in air under atmospheric pressure and in 0.01 Pa vacuum. (Colour on-line)

3.4 Mechanism of PL in as-prepared PPy

Based on theoretical and optical absorption studies, there are several allowed transitions in PPy depending on doping level [34]. In almost fully-reduced (undoped) PPy there is a strong absorption maximum associated with the interband transition (around 3.2 eV). In weakly doped PPy, there are three additional polaron-related features within the band gap: HOMO to lower polaron level (0.7 eV), lower to upper polaron level (1.4 eV), and HOMO to upper polaron state (2.1 eV) [34].

In the case of electrochemically prepared PPy the PL spectra in Fig. 1 or Fig. 6 before UV-modification show only the weak transition at around 400-420 nm (3.10 - 2.95 eV). This corresponds to interband transition. In the chemically prepared PPy before UV-modification, interband transition is missing and the weak broad-band low energy emission dominates the PL spectra. The broad background is most likely related with various defect states arising from imperfect polymerization in solution.

3.5 Mechanism of PL in UV-modified PPy

In spite of the initial PL spectra of electrochemically and chemically prepared PPy being different, they converge to the same new and intensive spectral band around 540 nm after UV irradiation. In the chemically prepared PPy, one can also notice additional corrugation that probably corresponds to polaron-related transitions [34]. That indicates that chemically prepared PPy is more conductive than electrochemical PPy. This is not surprising as PPy is expected to be doped by HCl and Cl^- ions are not washed out because the PPy is dropcasted onto substrate without any rinsing. Bipolarons are not involved in our considerations as they are associated with high doping of polymers that is expected to be low in our samples [18].

There are two possible explanations for the new PL band after the UV-modification. The first mechanism considers that the PPy PL can be caused by a transition between polaron (a charge carrier coupled to a local deformation of a polymer chain) and HOMO (highest occupied molecular orbital). On may say this is traditional interpretation, because it is based on theoretically predicted [34] and experimentally verified transitions typical for this material. If we assume that PPy band gap is about 2.95 eV (420 nm), as indicated by PL and transmittance measurements (Fig.1, Fig.2, Fig.6), maximum of the new PL band seems to match energetically with the theoretical prediction of difference between polaron and HOMO in weakly doped PPy [34]. However, ESR measurements revealed decrease of polaron and bipolaron concentration after UV modification of PPy [34]. Moreover, polarons in PPy are long-lived excitations that under normal circumstances recombine in a non-radiative way [38]. Thus the polaron-HOMO transition is unlikely to explain the high intensity of the new PL band.

We propose another, in our opinion more likely mechanism of the new PL band. It is based on adaptation of recombination mechanisms common for high luminescence polymers with non-degenerate ground state like PT and PPV [36]. It has been established that the main photoexcited species of these polymers are intra- and interchain excitons. Intrachain excitons or so-called polaron-excitons are weakly bound electron-hole pair coupled to local deformations of the conjugated backbone [37]. These singlet excitons are responsible for efficient radiative recombination. Interchain excitons are pairs of positive and negative polarons located on different polymer chains coupled to each other by Coulomb interaction. Such polaron pairs are long-lived non-radiative excitations [38]. Intensity and decay time of PL is directly linked to the ratio of these two competitive excitation and recombination mechanisms which depends on the distance of polymer chains, amount of defects and impurities, type of polymer, concentration of oxygen containing functional group, and others [33]. If we extrapolate results that were reported on PT and PPV, the new intensive PL band could be caused by radiative recombination of intrachain singlet excitons. Also this intrachain exciton-polaron model is consistent with the position of PL band. PPy Stokes shift between the band gap and maximum of intrachain emission band is about 0.8 eV. That is in a good agreement with magnitudes 0.6 eV to 0.9 eV reported for PT and PPV in dependence on preparation conditions and polymer type [37, 39]. Because not even minimal PL band around 540 nm is detected prior to the modification, the strong increase in PL intensity is due to an increased probability of singlet exciton generation rather than due to suppressed non-radiative channel of these species.

PL decay time is another characteristic of our samples supporting the proposed model. Generally reported photoluminescence decay time in these polymers is in the range from hundreds of ps to few ns [33, 37, 40]. This value fits to our measurement, presented in Fig. 5, that determine the decay time constant $\tau = 1.4$ ns. Moreover the PL time decay exhibits mono-exponential progress that is typical for intrachains excitons observed on PPV chains with low interchain interaction [31,41]. The reason why this PL band is not present in non-modified PPy could be caused by the strong interchain interaction. As a matter of fact almost all reported experiments resulted in PL on PPy were carried out on dissolved PPy [20,22].

Based on the above arguments and considerations, the model of PL mechanisms before and after UV-modification of electrochemically and chemically prepared PPy is schematically summarized in Fig.7. The model stresses the most pronounced PL transitions in each case and does not show relaxation and non-radiative transitions. Prior to the UV-modification of electrochemical PPy, the incident UV light is absorbed by PPy via generation of electron in LUMO and hole in HOMO. These carriers can radiatively recombine across the band gap or interact with polymer chain and create polarons which recombine mostly non-radiatively. Because the PL intensity is low, the polaron formation and non-radiative recombination is most likely dominating relaxation process. In the case of chemically prepared PPy the low energy transitions are most likely due to various defects in the material which dominate the weak PL response. Partially polaron-related transitions may also contribute as discussed above. The situation changes after the UV modification. The photogenerated charges create intrachain excitons that recombine radiatively with high efficiency. Additionally, small increase of band gap after UV modification is predicted as a reasonable consequence of absorption quenching (Fig.2).

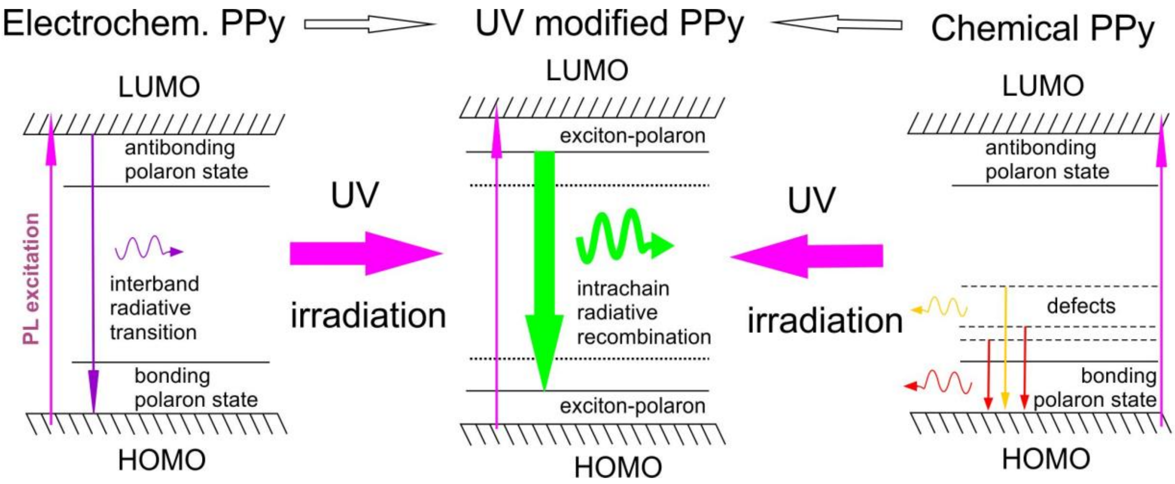

Figure 7. Model of photoluminescence mechanisms before and after UV-modification of electrochemically and chemically prepared PPy. (Colour on-line)

3.6. Origin of UV modification

Now the question is how new, exciton-related PL mechanism should arise after the UV-modification. As the modification is permanent, it must be related with a change of structure and/or chemical groups of PPy. We obtain a similar conclusion even from the analysis of absorbed photoenergy dissipation [44]. Phonons and lattice point defects can be created by UV light even at low light intensities so as the only one reasonable non-radiative channel remains photochemical modifications. These changes likely reduce PPy conjugation length that is followed by decrease of absorption as observed in Fig.2 [23, 31]. High efficiency of non-radiative recombination, that is typical for PPy, is also directly proportional to its conjugation length [17]. Intrachain excitons are naturally migrating to the parts of chains with the longest conjugation length before radiative recombination [17, 42, 43]. Chains with long conjugation length, increase probability of PL quenching site encounter. We are not implying that the decrease of conjugation length is the only reason for dramatic PL increase, because this kind of degradation is commonly created without presented phenomenon, but can notably magnify resulting effect. Such chemical and structural modifications of PPy after UV irradiation are supported by the XPS analysis in Table 1.

Table 1. Chemical composition of electrochemically and chemically prepared PPy on gold respectively quartz substrate before and after UV modification in air as determined by XPS.

Chemical composition [At%]	As-prepared electrochem. PPy	UV-modified electrochem. PPy	As-prepared chem. PPy	UV-modified chem. PPy
C1s overall	64.54	59.87	73.52	62.341
C1s sp2	5.31	7.71	21.24	20.29
C1s sp3	24.71	19.75	37.12	14.84
C1s C-N/C-O	17.36	12.02	8.17	7.51
C1s C=O/C=N	8.16	11.85	5.51	12.21
C1s N-C=O/O-C=O	8.76	8.26	1.49	7.16
C1s $\pi - \pi^*$	0.24	0.28	--	0.34
N1s	14.75	16.30	13.11	12.78
O1s	17.94	19.62	10.43	22.22
Cl2p	2.14	1.55	2.46	2.20
Na1s	0.29	1.24	0.48	--
Au4f	0.358	1.425	--	--
Si2p	--	--	0.48	0.47

Based on the above discussion and XPS data we propose two main UV-modification mechanisms. They are schematically shown in Fig. 8. The first mechanism is oxidation of carbon radicals generated in pyrrole ring without breaking it (Fig. 8a). It is natural conclusion from the necessity of air presence for efficient UV modification (Fig. 6) and was reported elsewhere [23]. The small increase of PPy PL even during UV irradiation in vacuum could be caused by reaction with adsorbed water. According to the XPS measurements the main demonstration of polymer oxidation is increase of C=O bonds that are being created during UV modification probably at the expense of π bonds between carbon atoms. Although as-prepared PPy samples showed different amount of oxygen for each preparation approach, all samples converted to the same state (about 20% of oxygen and 11% of C=O bonds) after UV modification. In case of chemically prepared PPy, new oxygen atoms are being integrated to the chain during modification and create C=O bond. On the other hand electrochemically prepared PPy already contains sufficient amount of oxygen in C-O bonds, that could convert to the C=O bond during UV irradiation.

The second mechanism is breaking of C-C bond between pyrrole rings and C-N bond followed by oxidation of the radicals (Fig. 8b). This is supported by the XPS data which showed decrease in C1s sp3 state and C1s C-N/C-O bonds. The decrease of carbon atoms in sp3 states could be partly explained by UV removing of impurities from PPy surface, because the ratio of C/N atoms is almost ideal for modified PPy in contrast to as-prepared samples, but cannot be the only reason for the reduction. Similarly the decrease of C1s C-N/C-O bonds cannot be explained only by transformation of C-O bonds to C=O. Presented mechanism is also in agreement with the fact that C-C bonds between the pyrrole rings are the weakest, followed by C-N bonds in the ring [45]. High binding energy of C-C bond can explain why UV light is necessary for the creation of the modification (Fig. 5) and is not thermally initiated. Moreover, this significant interference to the polymer structure will influence conjugation length of PPy that was proposed as an important factor for increasing PL intensity.

We expect that eventually it is being realized a combination of both mechanisms during the UV light irradiation. Moreover XPS analyze showed that UV irradiation decreasing doping level of PPy.

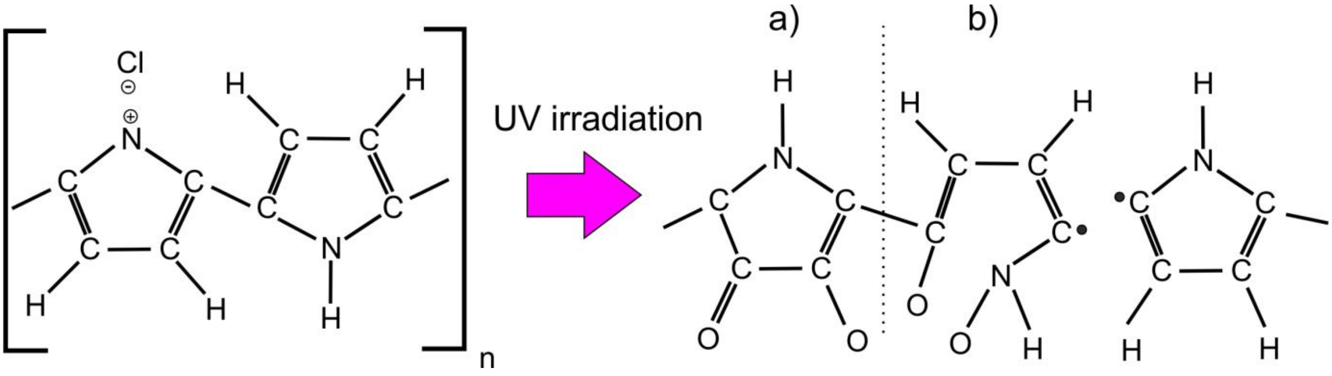

Figure 8. Structural model of PPy unit before and after UV modification. a) Oxidized pyrrole ring without carbon bond breaking. b) With C-C and C-N bond breaking.

Despite presented data and proposed interpretations of UV enhanced PL of PPy, further research is needed. More UV modification mechanism could be involved and for the exact determination of the polymer structural changes more experiments like FTIR is needed. Additional time-resolved measurements may contribute to better understanding of photoexcited species before and after modification. Photoluminescence spectroscopy of PPy under high pressure could determine of the influence of interchain interaction on radiative recombination. PL spectroscopy under low and high excitation intensity could indicate mono- or bi-molecular nature of radiative and non-radiative recombination of photoexcited species.

4. CONCLUSIONS

We have shown that PPy is modified by the UV light irradiation. Main result of the modification was increase in PL intensity with the maximum about 540 nm. The intensity increase reached more that 1000% of the original value before saturation. Based on the photoluminescence, absorption, and time-resolved spectroscopy we proposed model of UV enhanced PL recombination mechanism. Two possible interpretations are based on transition between polaron and valence band and radiative recombination of intrachain excitons which seems to be more likely mechanism. Regardless its origin, strong increase of PL after UV irradiation of PPy seemed to be sensitive tool for monitoring of polymer modifications and was used as a face value during additional experiments that were carried out for elucidate the nature of UV modification of our samples. We have proved that presented modifications are highly dependent on presence of air, cannot be induced thermally, and cause concentration changes of oxygen containing functional groups. We proposed the model of PPy structural and chemical modification that is based on UV-induced oxidation and/or breaking of PPy chains. The greatest advantage of the UV-induced PPy modification is that it works in the same way on PPy prepared by different methods and under various conditions. Observed phenomenon could be in the future used for selective UV patterning, intentional alteration of PPy properties or polymer protection.

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