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Itaco-perinone as a molecule with potential use in white light emitting materials. The effect of methyl- and methylene groups on the formation of perimidine and perinone structures

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ABSTRACT

New perimidine derivatives were synthesized via direct condensation between naphthalene-1,8-diamine and itaconic and citraconic anhydrides at low temperature. It was shown that substituent group in the anhydride had an important effect on pathway of the cyclization and the structure of the product. The target itaco-perinone molecule formed via double low temperature cyclization was found to have promising fluorescence properties emitting white light. Additionally, itaco-perinone was successfully copolymerized with styrene and methyl methacrylate via free radical mechanism and the ability to emit intensive white light from the polymer films was maintained.

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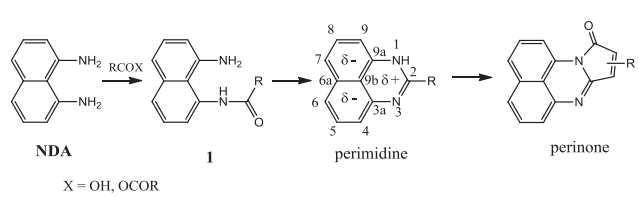
1. Introduction

Pyrroloperimidines or perinones are fused heterocyclic compounds and generally known as basis for various patented dyes and pigments recommended for wide range of industrial plastics, synthetic and natural fibers.[1–4] Owing to the highly conjugated structures these compounds have excellent resistance to heat and light and maintain the brightness of color even under plastic processing or long term sun exposure. Some of them, except bright color, show photoluminescence and thus may be promising materials for applications as luminescence sensors, organic light emitting diodes and other optoelectronic and analytical devices.[5–7]

The majority of the methods reported for synthesis of the perinones are based on condensation of naphthalene-1,8-diamine (**NDA**) with dicarboxylic acids or the corresponding anhydrides by refluxing in high boiling solvents or in aggressive acidic media.[3,8–10] The reaction proceeds by double cyclization via a monoacyl intermediate (**1**) and the formation of 2-substituted *H*-perimidine as the most probable product of the first cyclization step as shown in Scheme 1.[9–13]



Scheme 1. Synthesis of perinones from **NDA** and acid derivatives.

The arising interest in the perimidine-like structures in the last few years has been owned to their possible biological activities. Such various 1- and 2- substituted perimidines have been proposed as *anti*-fungal, *anti*-ulcer and *anti*-tumor agents.[10,12–14]

The 2-substituted perimidines are formed by condensation of **NDA** not only with acids and their derivatives (anhydrides, acyl chlorides), but also with other compounds containing carbonyl groups as aldehydes or ketones.[10–13] The ring-closure reaction with anhydrides is considered as the best synthetic route for the following reasons: (i) this method allows the formation of the product

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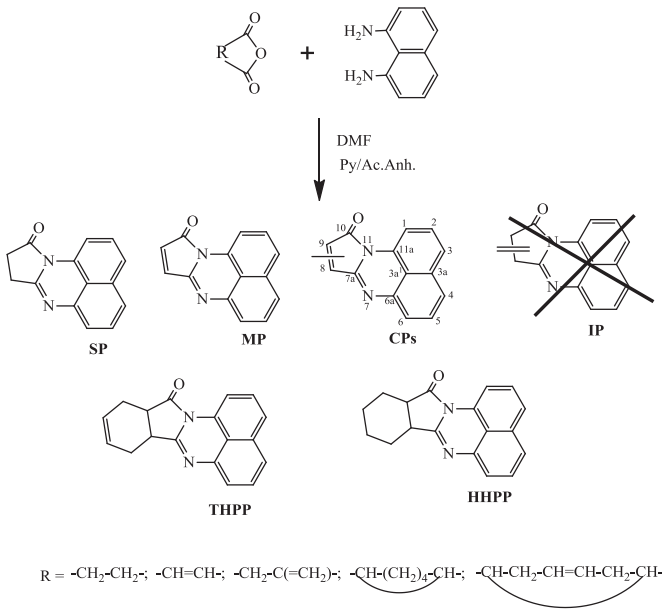
directly in one step in contrast to the reaction with aldehydes or ketones and (ii) has been seen to result in the highest yield and less contaminated product in comparison to the reactions with carboxylic acids or acyl chlorides. However, frequently reflux in acetic or trifluoroacetic anhydrides for several hours is needed for the cyclization. Recently, microwave-assisted synthesis has been developed, which decreased the reaction time and simultaneously increased the yields with both aliphatic and aromatic acids but high power oven (900 W) was used.[15]

Synthesis and *re*-arrangement of heterocycles have been a part of our interest for the search of new routes for synthesis of polyheteroarylenes.[16] The investigation of cyclization between acid anhydrides and aromatic diamines, such as *o*-phenylene diamine and **NDA**, resulted in synthesis of fused pyrrone and perinone frameworks, respectively at ambient temperature.[6] The route to perinones was particularly effective affording the products in very high yields (Scheme 2). Thus, using maleic, succinic, *cis*-1,2,3,6-tetrahydrophtalic and 1,2-cyclohexandicarboxylic anhydrides the corresponding perinones (**MP**, **SP**, **THPP** and **HHPP**) have been readily obtained. However, only citraco-perinones (**CP**s), in two isomeric forms differing from each other by the position of the methyl group (at the carbon atom 8 or 9, **CP-1** and **CP-2**, respectively) were formed from itaconic anhydride (**IA**), and so far no itaco-perinone (**IP**) has been obtained. The perinones with a carbon–carbon double bond in anhydride fragment were able to copolymerize with styrene (St) and methyl methacrylate (MMA) via free radical mechanism producing fluorescent polymers.[6] The reactivity of the perinones in the copolymerizations strongly depended on the position of the double bond and less conjugated **THPP** was easier to incorporate into the polymer chain than more conjugated **MP** and **CP**s. Therefore, it can be assumed that **IP** with a carbon–carbon double bond located outside the five-membered cycle should be much more active in the addition polymerization as it has been demonstrated for various itaconic derivatives, in comparison to the maleic ones.[17] Additionally, since the itaco-citraco isomerization occurs at significant rate above 50 °C,[18] **IP** could not be obtained using high temperature methods. Therefore, the low temperature approach is the only way to prepare this compound, but the reaction conditions need to be modified.



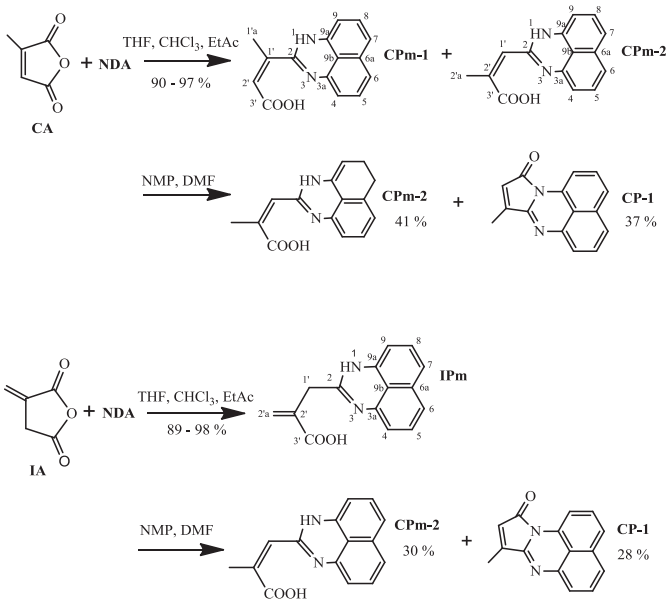
Scheme 2. Synthesis of perinones from **NDA** and diacid anhydrides at room temperature.

Herein we report the synthesis of the target **IP** and the influence of methyl- and methylene groups in the acid anhydride on the cyclizations and formation of perimidine skeletons. The electronic properties of the **IP** and its co-polymerization with MMA and St have also been studied.

2. Results and discussion

In our previous publication the majority of the synthesized perinones were obtained via single-stage method and the intermediate compounds were not fully characterized.[6] However, according to the numerous literature[11,19] it was logical to propose the formation of the corresponding monoacylated intermediates (**1** in Scheme 1) as principal products of the reactions between **NDA** and the anhydrides, when used in equimolar amounts before the addition of the dehydrating agent. As mentioned above, elevated temperatures or/and acidic conditions are required for the synthesis of the perimidines. Thus, the reaction between **NDA** and strongly dehydrating trifluoroacetic anhydride resulted in the formation of 2-trifluoromethylperimidine at low temperature when 10-fold excess of the anhydride was used. If the same reaction was carried out with equimolar amounts of the reagents, the corresponding monoacyl compound was obtained.[19a]

With the aim of finding the conditions for the synthesis of **IP** we have studied in detail the reactions of **NDA** with **IA** and its isomer, citraconic anhydride (**CA**). The results are shown in Scheme 3.



Scheme 3. Condensations of **NDA** with **IA** and **CA** in different solvents. Conditions: room temperature, 2 h. The yields were determined on isolated products.

2.1. Citraco- and itaco- perimidines

It has already been demonstrated that the condensation of **NDA** with **IA** in the presence of dehydrating acetic anhydride/pyridine mixture resulted in two isomeric forms of citraco-perinone, **CP-1** and **CP-2**, but not in the desirable **IP** (Scheme 2).[6] Analyzing the reactions step by step we have found that the perimidine framework is readily formed in low polar solvents with both, **IA** and **CA**, anhydrides without any heating or the addition of a dehydrating agent (Scheme 3). The perimidines precipitated directly from the reaction mixture as pale-yellow or reddish powder for itaco- and citraco-derivatives, respectively. The reactions were carried out in the temperature range from −78 to 25 °C; and the corresponding

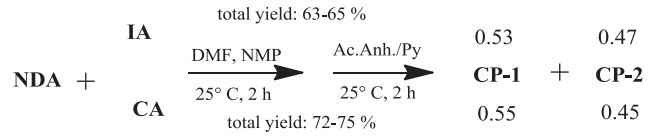
perimidines were always obtained practically in quantitative yields; no monoacylated derivatives were isolated even at −78 °C. The perimidines synthesized were poorly soluble even in organic solvents such as DMF, NMP and DMSO. The ^{1}H and ^{13}C NMR spectra of the product of the condensation with **IA** were quite simple and resemble those of 2-substituted *H*-perimidines, with the characteristically upfield shifted H4 and H9 protons.[10–13,20] As a consequence of the degenerate tautomerism the aromatic carbons and protons in positions 4 and 9, 5 and 8, 6 and 7 become equivalent. Thus, based on the NMR data together with results of mass analysis and IR spectrum the sole reaction product was identified as 2-acrylic acid perimidine (**IPm**). The reaction between **NDA** and **CA** under the same conditions resulted in two perimidines differing by the position of the methyl group either at 10 (**CPm-1**) or 11 (**CPm-2**) carbon atom, similar to the perinone isomerism (**CP-1** and **CP-2)** previously reported.[6] The isomers were formed almost in equal proportion at room temperature, the **CPm-1**:**CPm-2** molar ratio=0.57:0.43, was independent of the solvent, but the amount of **CPm-1** isomer increased with decreasing temperature as shown in Table 1. For example, the reaction at 0 °C produced the mixture with a molar ratio **CPm-1**:**CPm-2**=0.73:0.27, while at −78 °C the molar fraction of **CPm-1** practically reached 90%. Such temperature dependence suggested that the isomer **CPm**-1 is a kinetically favorable product and **CPm-2** is thermodynamically favorable.[21]

Table 1
Influence of the temperature on the composition of **CPm** mixture obtained in condensation of **NDA** with **CA** in $CHCl_3$

T, °C	Total yield, %	CPm-1/CPm-2 M ratio
25	97	0.57/0.43
0	95	0.73/0.27
−78	92	0.87/0.13

When the same reaction between **NDA** and the anhydrides, both **IA** and **CA**, was carried out in polar NMP or DMF two fused heterocycles resulted from the first (perimidine) and secondary (perinone) cyclizations were obtained in quite similar yields. The perimidines were separated by simple filtration from the reaction mixture; and the perinones were isolated as a precipitate after pouring the dark red mother liquid in cold water. Only citraco-forms were obtained from **IA** meaning that polarity of the solvent may even be more important factor than the amine basicity for the itaco-citraco isomerization, as has been generally assumed.[18] Interestingly, only one isomeric form of each products, namely **CPm-2** and **CP-1**, were formed under these conditions. This coincides with our conclusion on a higher thermodynamic stability of the **CPm-2** isomer, meanwhile less stable **CPm-1** undergoes further dehydration producing the **CP-1** perinone. It is noteworthy that cyclization of **CPm-1** to **CP-1** took place even in the solid state during the storage of the product, obviously but the process was much slower. Thus, the secondary cyclodehydration partially proceeded in polar solvents at room temperature without any dehydrating agents. However, the targeted **IP** could not be obtained under these conditions because of the fast itaco-citraco isomerization occurring even before the first cyclization step.

This data is in good agreement to the results obtained when the cyclization to the perinones was performed in the presence of acetic anhydride/pyridine dehydrating mixture in one stage without isolation of intermediates as shown in Scheme 4. Both **CP-1** and **CP-2** were obtained in practically equal amounts with only a small excess of the **CP-1** isomer. The dehydrating mixture was mainly used for the cyclodehydration of the more stable **CPm-2**.



Scheme 4. One-pot condensation of **NDA** with **IA** and **CA** in polar solvents.

2.2. Theoretical considerations

To get deeper insight into the reaction mechanism the elemental steps of some of the above mentioned transformation have been studied using quantum chemistry tools. Our goal was to evaluate influence of methyl- and methylene substituent groups in anhydride on the cyclization reactions. Thus we studied the reaction pathway from the amic acid, as the first intermediate in the reaction between the diamine and diacid anhydride (**1** in Scheme 1), to the corresponding perimidines for non-substituted maleic anhydride (**MA**), and substituted **CA** and **IA**. The attack of nitrogen atom of free amino-group at carbonyl carbon, is the rate determining step for the cyclization. The calculations showed that the Gibbs free energy of activation for formation of **CPm-1** is 3.0 kcal/mol lower compared to that for the formation of non-substituted malei-perimidine. The difference in the activation energies between these very similar compounds is related to the higher stability of the non-substituted amic acid intermediate because of strong hydrogen bond between amide carbonyl and hydroxyl group. As can be seen from Fig. 1 such conformation cannot be adopted by the methyl-substituted intermediate due to steric hindrance caused by the methyl group. As a result the cyclization of the amic acid produced from **CA** should occur easier.

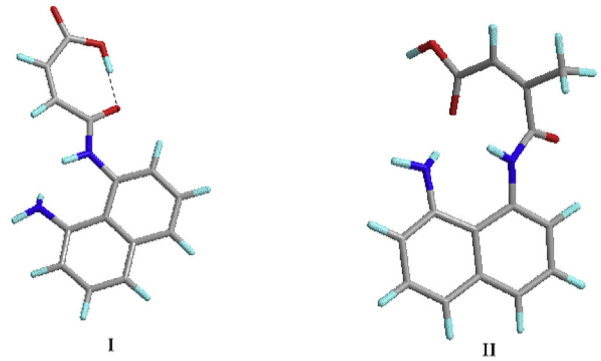


Fig. 1. The lowest energy conformations for amic acids formed from **NDA** and anhydrides, maleic (**I**) and citraconic (**II**).

The cyclodehydration reaction of **CPm-1** and **CPm-2** leads to the corresponding methyl-10*H*-pyrrolo[1,2-*a*]perimidin-10-ones, **CP-1** and **CP-2**. And, again, much easier formation of **CP-1** is accounted for the influence of the methyl group. The optimized geometries of the rate limiting transition states (TS) for the formation of the perinones, **TS-CP-1** and **TS-CP-2**, are depicted in Fig. 2. The **TS-CP-1** is 2.7 kcal/mol lower in the Gibbs free energy compared to **TS-CP-2**. This difference can be explained by the repulsion between lone pare of the pyrimidine nitrogen atom and methyl group in **TS-CP-1** that facilitates the ring closure. There is no such assistance for the ring closure in **TS-CP-2** resulting in the higher activation energy process.

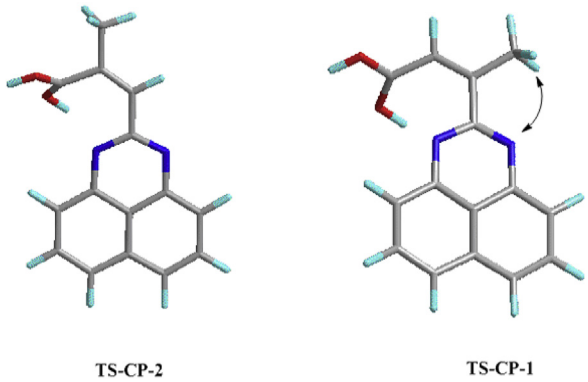
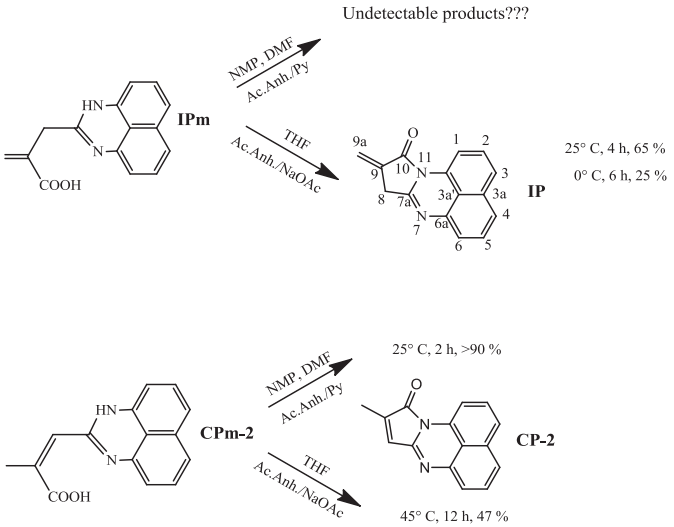


Fig. 2. Optimized transition state structures for the formation of citraco-perinones.

2.3. Itacoperinone

Since **IPm** was the only appropriate intermediate for the following synthesis of the target **IP** we started to search for the conditions of its cyclization under, which the carbon–carbon π-bond in the anhydride fragment would not be affected. The results are summarized in Scheme 5.



Scheme 5. Cyclodehydration of itaco- and citraco-perimidines to the corresponding perinones.

At first we tried to obtain **IP** skeleton using the traditional acetic anhydride/pyridine dehydrating mixture in amidic solvents because in contrast to **IA** the itaco-perimidine was very stable and according to DSC analysis did not undergo so readily itaco-citraco rearrangement at heating as **IA**. The reaction was clearly observed under these conditions, the insoluble **IPm** disappeared giving dark-red homogenous solution. The product as a red powder was isolated by filtration after precipitation in cold water in quite high yield, but we could not determine its structure. The ^{1}H NMR spectrum of the dry crude product showed very broad ill defined signals, no resonances from methylene- or methyl-protons were observed. Mass analysis showed peaks from various molecular ions, one of them corresponded to mass of the perinone. Attempts to purify by recrystallization or by column chromatography (silica), techniques effectively applied for purification and separation of **CP**s, were unsuccessful. The product did not form crystals and only **CP-2** was isolated as a result of the chromatography but in minor amount (less than 10%).

For comparison, the cyclization of **CPm-2**, an isomeric form of **IPm**, was also carried out under the same conditions. Similarly, dark-red homogeneous solution was obtained and the product was isolated by filtration after precipitation in water; it was dried to a constant weight and without further purification analyzed by NMR spectroscopy. According to the ^{1}H NMR data it was identified as **CP-2** compound of very high purity, no other signals, except those from **CP-2**, were seen in the spectrum.

Then, other cyclization conditions were applied using an acetic anhydride/NaOAc dehydrating mixture in THF to lower the basicity and polarity of the reaction system.[22] Since the dehydrating capacity of acetic anhydride/NaOAc is weaker the temperature was increased to 50 °C because the cyclization proceeded very slow at lower temperatures while higher temperatures increased the possibility of itaco-citraco isomerization.[18a] Thus, the pale orange-reddish powder was obtained after the appropriate reaction treatment; the ^{1}H NMR spectrum of the dry crude product contained, except the aromatic resonances, two intense signals from methylene protons at 5.70 and 6.39 ppm, presumably due to the presence of itaco-perinone compound in an important amount. However, the purification was problematic again; after the column separation only citraco-perinone was isolated in very low yield (~8%), but not its itaco-isomer. It was assumed that **IP** was not stable enough under the chromatography conditions and its purification turned out to be a difficult task. Therefore, we decided to decrease the reaction temperature in order to suppress the side reactions and obtained much more pure **IP**. And, indeed, practically pure **IP** was obtained as an orange powder at room temperature after 4 h; the yield of 65% was reasonably good but not as high as for the citraco-isomers using acetic anhydride/pyridine mixture. Prolongation of the reaction time to 8 h did not lead to a significant increase in the **IP** yield and, moreover another product started to form. We also carried out the cyclization at 0 °C, but the reaction was too slow. Interestingly, the conversion of **CPm-2** into **CP-2**, which was very fast and efficient using acetic anhydride/pyridine mixture at room temperature, barely proceeded in the presence of acetic anhydride/NaOAc dehydrating agent. The reaction was slow even at 45 °C producing less than 50% yield after 12 h. Therefore the substituent plays very important role in the cyclization mechanism.

2.4. Electronic absorption and emission spectra

Perimidines rarely luminescence on irradiation with UV light, only a few photo-emitting perimidine-based compounds are known to the date,[10–13,23] and one of such examples is luminescent pyrrolo-perimidines previously reported by our group.[6] Thus, electronic absorption and emission properties of the perimidines synthesized were studied and the main results are summarized in Table 2. Typically, the electronic absorption spectra of perimidine system consists of two highly intense broad bands with maxima at approx. 230 and 330 nm, which are related to the electronic transitions within naphthalene ring and the transfer of the electron pair of the nitrogen to the antibonding π orbital of the naphthalene, respectively.[10,11,13] Frequently, the third low intense absorption related to charge-transfer between the naphthalene ring (π-donor) and hetero-cycle (π-acceptor) is also manifested as a shoulder at 400 nm (most perimidines are of bright yellow color) but its position may vary depending on the 2-substituing group.[10,11,24] Since **CPm**s and **IPm** were poorly soluble in organic solvents their spectral characteristic were studied in DMSO but even in this solvent the solubility was very limited. UV–vis spectrum of **IPm** was quite typical for perimidine framework showing the main absorption at 330 nm with long-wave shoulder at 380 nm explaining its pale-yellow color. Unfortunately, the short-wave band could not be seen because of DMSO absorption in this region. In comparison to the electronic spectrum of **IPm**, the absorption bands of **CPm** were

Table 2
UV–vis absorption and emission spectral data of the perimidine and perinone compounds

Compound	Absorption, nm ($\varepsilon_{max}\times10^{-3}$, L mol^{-1} cm^{-1})	Emission, nm	Quantum yield, Φ_{fl}
CPms	351 (12.4) 460 (3.6)	—	—
IPm	334 (10.9) 380 sh.	610	0.004
IP	245 (21.3) 371 (11.1)	560	0.13
CPs	230 (46.1)[a] 293 (15.6) 480 (6.6)	No	
SP	245 (16.8) 332 (8.9)	470	0.10

The absorption spectra of **CPm**s and **IPm** were run in DMSO and their emission spectra in MEOH. The spectra of perinones were measured in $CHCl_3$.
[a] This band was not seen in $CHCl_3$, the data measured in MeOH is taken from Ref. 6.

red shifted; the main absorption was observed at 350 nm while another band of much lower intensity at 460 nm. Such difference in the spectra between **IPm** and **CPm** may be explained by influence of the carbon–carbon double bond in the anhydride fragment on the heterocycle. In **CPm**s the C=C bond enters in conjugation to the C=N bond of the heterocycle, while the C=C bond of **IPm** is separated by distance of two σ-carbon–carbon bonds from the heterocycle.

The spectral features of **IP** were compared to those of the previously described[6] similar perinones, **CP**s and **SP** (Table 2). The UV–vis absorption spectrum of **IP** showed only two principal bands at 245 and 370 nm. These bands are strongly bathochromically shifted in comparison to the absorptions of **CP**s, and the longest wavelength charge-transfer absorption at 480 nm, which is characteristic of **CP**s, was not observed for **IP**. Therefore, the positions and extinction coefficients of the **IP** absorption bands are more similar to the spectral data of less conjugated **SP** than the spectrum of isomeric **CP**s.

Furthermore, similar to **SP**, the **IP** molecule also emitted visible light. In fact, both itaco-derivatives, **IPm** and **IP**, fluoresced although the intensity of the fluorescence of **IPm** was very low (see Table 2). **CPm**s did not show any notable luminescence that coincides with the results for completely cyclized **CP**s.[6] On the contrary, fluorescence of **IP** was of relatively high intensity and, more importantly, **IP** emitted white light with a maximum intensity at 560 nm, meaning that the emission was broad and covered practically the whole visible region from 390 to 700 nm. The above is illustrated by results presented in Table 2 and insets (a) and (b) of Fig. 3.

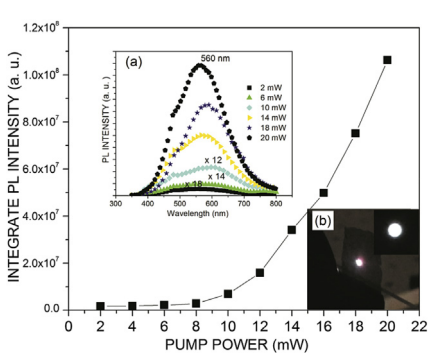


Fig. 3. The exponential tendency of the integrate photoluminescence (PL) intensity of poly(MMA-*co*-**IP**) film, containing 0.6 mol % of **IP**, with respect to the laser power. Insets show (a) the whole PL spectrum and (b) the intense spot emission of the copolymer.

2.5. Copolymerization of IP

Organic luminescent materials are generally preferred over their inorganic counterparts owing to their low cost, solution processability, flexibility and etc.[25] Current trends in artificial lighting have boosted the demand for white organic light-emitting materials, because in most cases, white-light emitting diodes are made of combination of individual compound emitting in red, green and blue area of spectrum.[25,26] Although considerable progress has been made in this field, development of purely organic white-light emitting materials of simple structure still remains very urgent task. Thus, **IP** is a promising molecule from this point of view. Since, very frequently the generation of white-light is limited to solution state, **IP** was tried in co-polymerization with styrene (St) and methyl methacrylate (MMA). This was actually our principal stimulus for the synthesis because the non-conjugated exocyclic methylene in **IP** was expected to co-polymerize readily with these traditional monomers. And, indeed, **IP** could be successfully introduced into the polymer chains via free radical mechanism. The details of the co-polymerization are currently under investigation, but flexible polymer films were obtained and we would like to report that the **IP** molecules being even chemically incorporated into the polymers, keep the ability to emit white light intensively. Fig. 3 shows the features of photoluminescence of the copolymer of MMA with **IP** (1 mol % in the monomer feed); the emission spectrum of the copolymer and the picture of the emitting sample are given as insets (a) and (b) correspondingly. The emission spectrum of poly(St-*co*-**IP**) looked very similar. Additionally, the influence of laser power on the luminescence intensity of the copolymers has been investigated at room temperature. The data is presented in Fig. 3 as a plot of the integrated photoluminescence intensity versus pump power. Pump power has been varied from 2 mW until 20 mW with the step of 2 mW. It is important to note that there is an exponential increase of the integrated luminescence as a function of laser power, which clearly demonstrates a tendency to optical gain of this material.[27]

3. Conclusions

In conclusion, the reaction between **NDA** and isomeric **CA** and **IA** resulted in a formation of the 2-substituted perimidines in quantitative yields at low temperature without any dehydrating agent. The solvent nature and substituent group had an important effect on the structure of the products. The efficient route for synthesis of the new **IP** molecule has also be found. **IP** turned out to be luminescent with the broad emission spectrum covering the whole visible region. Additionally, **IP** could be readily copolymerized with MMA and St maintaining its ability to emit white light intensively from the polymer films. Thus, **IP** may very promising compound for development of new organic light emitting devices.

4. Computational details

All calculations were carried out using a robust M06-2X functional[28a] in combination with large def2-TZVPP basis set.[28b] SMD continuum solvation model[28c] was used to take into account solvent effect of THF—the reaction media. Gaussian 09 rev D.01 suite of programs[28d] has been used for all calculations. For all systems frequency calculations were run to ensure that a minimum (0 imaginary modes) or a transition state (1 imaginary mode) have been located.

5. Experimental

5.1. General

Starting materials, reagents and solvents were supplied by Aldrich. 1,8-diaminonaphtelene (**NDA**) was recrystallized from ethanol, methyl methacrylate (MMA) and styrene (St) were passed through a column filled with neutral alumina prior to use. All other chemicals were used as received. Thermal analysis were performed on TA Instruments Thermogravimetric Analyzer, Model Q5000IR, and TA Instruments Differential Scanning Calorimeter, Model DSQC 2000 at a heating rate of 20 °C/min. UV–vis spectra were recorded on a Varian Cary 400 UV–vis spectrophotometer. Fluoresce spectra in solutions were recorded on a Perkin–Elmer LS50B fluorescent spectrometer with Rhodamin 6G as a standard. Photoluminescence spectra of the copolymer samples were obtained using a Kimmon Koha He–Cd laser with λ_{exit}=325 nm and output power was varied from 2 mW to 20 mW, at room temperature. The sample emission was focused into an Acton SpectraPro 2500i spectrograph and detected by a photomultiplier tube. All the spectra were corrected taking into account the spectral response of the system. Infrared spectra were recorded on a Bruker Alpha-P ATR FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded either on Varian Unity Inova 500 MHz spectrometer or on Bruker Avance III 400 MHz spectrometer in $CDCl_3$ for perinone and DMSO-d_6 for perimidines. The peaks from residual non-deuterated solvents ($CHCl_3$: 7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C) (DMSO: 2.54 ppm for ^{1}H and 40.5 ppm for ^{13}C) were used as the internal references. For detailed peak assignments DEPT 90, Dept 135 and 2D spectra were run (^{1}H–^{1}H COSY, HSQC, HMBC). High-resolution mass spectra were measured on Jeol JMS T100LC with an IonSense Direct Analysis Real Time (DART). The molecular weights and the molecular weight distributions of the polymers were determined by GPC with THF eluent at 35 °C using a Waters 2695 ALLIANCE Separation Module equipped with a RI Waters 2414 detector and two HSP gel columns (HR MB-L molecular weight range from 5×10^2 to 7×10^5 and MB-B from 10^3 to 4×10^6).

5.2. Synthesis of 2-substituted *H*-peremidines

The perimidines were synthesized via condensation of **NDA** with the corresponding anhydride taken in equimolar amounts. Most of the reactions were carried out at room temperature, but several condensations in $CHCl_3$ were conducted at −78 °C (acetone/dry ice cooling bath), −10 °C (ice/NaCl cooling bath) and 0 °C. The details are described below. All the structures synthesized were characterized by NMR (^{1}H and ^{13}C), FTIR, UV–vis and mass-spectroscopies and thermal analysis. The yields were determined on isolated products.

*5.2.1. Itaco-perimidine (**IPm**, IUPAC name 2-((1H-perimidin-2-yl) methyl)acrylic acid).* Itaconic anhydride (1 g, 0.004 mol) was added to a solution of **NDA** (0.6328 g, 0.004 mol) in 50 mL of chloroform, THF or ethyl acetate and the reaction mixture was stirred for 2 h. A pale yellow powder precipitated from the reaction mixture was filtered off, than washed with ethanol (200 ml) at continuous stirring for another 1 h in order to remove the unreacted residues, then filtered off again and dried in vacuum to a constant weight. The yields were 98% in $CHCl_3$ and 89% in THF, and EtAc at room temperature. Slightly lower yield of 92% in $CHCl_3$ was obtained at −78 °C; mp=215 °C; IR (ATR): 2100–3100 (hydrogen bonds), 1657 (C=O), 1548 (C–N) cm^{-1}; ^{1}H NMR (400 MHz, DMSO, δ, ppm): 3.24 (s, 2H)(1′), 5.76 (d, J=1.4 Hz, 1H)(2a′), 6.16 (d, J=1.4 Hz, 1H)(2a′), 6.37 (dd, J=7.4, 0.9 Hz, 2H)(4 and 9), 6.97 (dd, J=8.4, 0.9 Hz, 2H)(6 and 7), 7.08 (dd, J=8.3, 7.4 Hz, 2H)(5 and 8); ^{13}C NMR (101 MHz, DMSO, δ, ppm): 167.5 (quart)(3′), 155.3 (quart)(2), 141.6 (3a and 9a)(quart), 136.3 (quart), 135.1 (quart)(6a), 128.2 (*tert*)(5 and 8), 126.9 (*sec*)(2a′), 121.4 (quart)(9b), 118.1 (*tert*)(6 and 7), 107.3 (*tert*)(4 and 9), 37.1 (*sec*)(1′); HRMS (DART$^+$) calcd for [$C_{15}H_{13}N_2O_2$] 253.0977 found 253.09762.

*5.2.2. Citraco-perimidines (**CPm**s, IUPAC names (Z)-3-(1H-perimidin-2-yl)but-2-enoic acid, **CPm-1**, and (Z)-2-methyl-3-(1H-perimidin-2-yl)acrylic acid, **CPm-2**).* These perimidines were obtained analogously but using citraconic anhydride. In difference to **IPm** the product was of pale reddish color. The total yields were 97% in $CHCl_3$ and 90% in THF, and EtAc; mp=221.5 °C; IR (ATR): 2200–3048 (hydrogen bonds), 1651 (C=O), 1587 (C–N) cm^{-1}; ^{1}H NMR (400 MHz, DMSO, δ, ppm) for CPm-1: ^{1}H NMR (300 MHz, DMSO, δ, ppm): 2.11 (s, 3H)(1a′), 6.01 (s, 1H)(2′), 6.42 (d, J=7.2 Hz, 2H)(4 and 9), 7.02 (d, J=8.3 Hz, 2H)(6 and 7), 7.12 (dd, J=7.2 Hz, 2H)(5 and 8) and for CPm-2: 2.07 (d, J=1.4 Hz, 3H)(2a′), 6.26 (d, J=1.4 Hz, 1H)(1′), 6.47 (dd, J=7.1, 1.0 Hz, 2H)(4 and 9), 7.13 (dd, J=8.4, 0.9 Hz, 2H)(6 and 7), 7.19 (dd, J=8.3, 7.2 Hz, 2H)(5 and 8); ^{13}C NMR (101 MHz, DMSO, δ, ppm) for CPm-1: 165.1 (quart)(3′), 154.8 (quart)(2), 145.4 (quart)(1′), 140.9 (quart)(3a and 9a), 134.9 (quart)(6a), 127.9 (*tert*)(5 and 8), 122.6 (*tert*)(2′), 121.5 (quart)(9b), 118.1 (*tert*)(6 and 7), 107.3 (*tert*)(4 and 9), 22 (CH_3)(1a′) and for CPm-2: 166.9 (quart)(3′), 151.8 (quart)(2), 146.8 (quart)(2′), 137.9 (quart)(3a and 9a), 134.9 (quart)(6a), 128.6 (*tert*)(5 and 8), 122.7 (*tert*)(1′), 121.2 (quart)(9b), 119.9 (*tert*)(6 and 7), 107.5 (*tert*)(4 and 9), 24.3 (CH_3)(2a′); HRMS (DART$^+$) calcd for [$C_{15}H_{13}N_2O_2$] 253.0977 found 253.09769.

5.2.2.1. This compound was obtained as a reddish precipitate in the reaction of **NDA** with **CA** or **IA** using the same procedure as described in Section 2.2 but in polar amidic solvents, DMF or NMP. Analogously the precipitate was filtered off, washed with ethanol and dried. The yields were 40 and 30% for **CA** and **IA**, respectively. **CP-1** was formed as precipitate after pouring mother liquid in cold water.

5.3. Itacoperinone (IP, IUPAC name 9-methylene-8*H*-pyrrolo [1,2-a]perimidin-10(9*H*)-one)

IPm (1 g, 0.004 mol) was added to 120 ml of THF with sodium acetate (0.278 g, 0.001 mol), then acetic anhydride (5 mL, 0.053 mol) was added and the mixture was stirred for 4 h at room temperature. Then unreacted **IPm** was filtered off and the mother liquid was poured in water (200 ml) and neutralized with sodium bicarbonate. The orange precipitate was filtered off, washed with water and dried in vacuum to a constant weight. The yield was 65%; mp≈145 °C (the endortherm overlaps with the exotherm of isomerization); IR (ATR): 1739 (C=O), 1663 (C=N), 1583 (heteroc. syst.), 1403 (C–N) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 3.55 (t, J=2.5 Hz, 2H)(8), 5.70 (t, J=2.3 Hz, 1H)(9a), 6.39 (t, J=2.7 Hz, 1H)(9a), 7.04 (dd, J=7.1, 1.1 Hz, 1H)(6), 7.32 (td, J=8.1, 2.3 Hz, 2H)(2 and 5), 7.36 (dd, J=8.3, 1.0 Hz, 1H)(4), 7.44 (dd, J=8.3, 0.6 Hz, 1H)(3),8.31 (dd, J=7.7, 0.8 Hz, 1H)(1). ^{13}C NMR (126 MHz, $CDCl_3$ δ, ppm): 166.1 (quart)(10), 153.5 (quart)(7a), 139.4 (quart)(6a), 134.2 (quart)(3a), 133.1 (quart)(9), 131.8 (quart)(11a), 128.1 (*tert*)(5), 127.3 (*tert*)(2), 123.9 (*tert*)(3), 123.6 (*tert*)(4), 120.9 (*sec*)(9a), 119.8 (quart)(3a′), 118.8 (*tert*)(6), 109.8 (*tert*)(1), 31.1 (*sec*)(8); HRMS (DART$^+$) calcd for [$C_{15}H_{11}N_2O$] 235.08714 found 235.08703.

5.4. Copolymerizations of IP with MMA and St

The initial monomer feeds containing 0.5, 1.0, 3.0 and 5.0 mol % of **IP** were used for co-polymerizations. The polymerizations were carried out in bulk under N_2 using AIBN (0.1 M) as radical initiator at 80 °C for MMA and 110 °C for St. The monomer conversion was

determined gravimetrically. The co-polymerizations with MMA were stopped after 120 min by cooling and the conversions of 48% (**IP**/MMA=0.5/99.5), 32% (**IP**/MMA=1/99) and 14% (**IP**/MMA=3/97) were obtained. The copolymerizations with St were stopped after 180 min that resulted in conversions of 44% and 16% for **IP**/St=0.5/99.5 and **IP**/St=5/95 feeding compositions correspondingly. In order to remove the unreacted **IP** the copolymers obtained were dissolved in THF and then precipitated in methanol. The procedure was repeated several times untill no absorption bands related to **IP** were observed in UV–vis spectrum of the methanol used for the precipitation. The copolymers were characterized by GPC and ^{1}H NMR techniques. The molecular weight characteristics were the following: (i) for poly(MMA-*co*-IP) Mn=109,000 and Mw/Mn=2.04 (**IP**/MMA=0.5/99.5); Mn=86,000 and Mw/Mn=2.17 (**IP**/MMA=1/99); Mn=11,000 and Mw/Mn=2.23 (**IP**/MMA=3/97); (ii) poly(St-*co*-IP) Mn=45,000 and Mw/Mn=2.36 (**IP**/St=0.5/99.5); Mn=3,000 and Mw/Mn=2.40 (**IP**/St=5/95). The ^{1}H NMR spectra of the copolymers with 3.0 and 5 mol % of **IP** are given in Supplementary data. The amounts of **IP** in the co-polymers were evaluated using the absorption at 370 nm in the electronic spectra. Thus, for the monomer feeds of **IP**/MMA=1/99 and 3/97 the amount of **IP** in the copolymers were 0.6 and 2 mol %, respectively; for the feeds IP/St=0.5/99.5 and 5/95 the amount of **IP** in the copolymers were 0.36 and 3.5 mol %, respectively.

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Supplementary data

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