Tuning the Luminescence of Polyacrylonitriles by Controlled Polymerization

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Abstract

Nonconventional luminescent polymers (NCLPs) have attracted considerable attention due to their unique luminescence behavior. Although various routes can be employed to synthesize such vinyl-based NCLP, the dependence of their photophysical properties on the polymerization method used and thus potential small variations of the overall macromolecular architecture is rarely reported. In this study, we have investigated in detail the luminescence behavior of polyacrylonitriles (PANs) synthesized with two different polymerization methods, namely by free-radical polymerization (FRP), and reversible addition-fragmentation chain transfer (RAFT). Dependent on the polymerization route and initiator used, the PANs show distinct PL and excitation wavelengths, and their emission covers a wavelength range from 400 to 630 nm, respectively. Moreover, the synthesized PANs easily can be homogeneously blended both in solution and solid states, and the resulting emission is a superposition of the emission of the blend components. This study provides a facile approach to tune the photophysical properties of PANs and related vinyl-based NCLPs and provides new fundamental insight to further booster application development of NCLPs.
Introduction

Recently, non-conjugated polymers with intrinsic photoluminescence (PL) have attracted considerable attention.\textsuperscript{1, 2} Generally, these nonconventional luminescent polymers (NCLPs) consist of certain subgroups, such as acylamino (-NH-CO-), carbonyl (C=O), hydroxyl (-OH), or cyano (C≡N).\textsuperscript{3-9} It is generally accepted that the emission of NCLPs is due to the clustering of non-conjugated chromophores and through space conjugation (TSC) effect, namely, clustering-triggered emission (CTE).\textsuperscript{1,8,10-15} By taking advantage of the straightforward processability of polymers, NCLPs have potential for applications in anti-counterfeiting, sensors, bioimaging, etc.

Polymerization is the process to create polymers, and the chosen polymerization route and conditions determine the fundamental features of a polymer, including composition, configuration, molecular weight, dispersity, and functionalization, to name but a few. To date, most of the NCLPs are vinyl-based polymers, such as poly(N-vinylpyrrolidone) (PNVP),\textsuperscript{3} poly(maleic anhydride) (PMAh),\textsuperscript{4, 5} poly(itaconic anhydride) (PITA),\textsuperscript{6, 7} poly(N-vinylcaprolactam) (PNVC),\textsuperscript{16} and polyacrylonitrile (PAN).\textsuperscript{8, 9} One of the most common and useful reactions for synthesizing vinyl polymers is free-radical polymerization (FRP), in which an initiator is employed to start the reaction. Besides, to achieve polymers with well-controlled features, controlled radical polymerization (CRP) techniques are developed, such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization.\textsuperscript{17-23} With the utilization of CRP, not only the molecular weight and dispersity of polymers can be well-controlled, but also their architectures can be designed and constructed. Therefore, various polymeric materials, including block copolymers, polymer brushes, and polymer bioconjugation, can be synthesized by using CRP techniques.\textsuperscript{24}

CRP is able to alter the overall molecular architecture in a controlled way, down to very small molecular variations. We expect that such differences of the molecular architecture will influence the optical properties of the NCLP, and particularly the
clustering-triggered emission. As one of the few reports on utilizing CRP for NCLPs synthesis, recently, Zhang and coworkers demonstrated for poly(maleimide)s full-color luminescence.\textsuperscript{25}

In our study, for the first time, we have altered the photophysical properties of NCLPs by utilizing different radical polymerization methods. We have used PAN as a typical NCLP model polymer.\textsuperscript{8, 9, 26} Our results show that all the PANs exhibited PL emission in both solution and solid state, and that their emission properties are determined by the polymerization route used. Moreover, we show that, by simple blending of different PANs, the PL color range is extended. This study provides a facile approach to tune the photophysical properties of PANs, and gives fundamental insight into the development and application of NCLPs.

2. Results and discussion

2.1 Synthesis of PANs

To investigate the impact of polymerization methods on the photophysical properties of PAN, we synthesized PAN samples via FRP and RAFT (Scheme 1). The experimental conditions are shown in Table 1, and more details can be found in the Experimental Section. Firstly, PANs were synthesized by FRP by using various initiators and chain transfer agents (CTAs), which were termed as F1-F4 (Table 1). The polymerization of F1 and F2 was initiated by AIBN, and 1-dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{-SH}$) was used as CTA. F3 and F4 were prepared by using (NH$_4$)$_2$S$_2$O$_8$ and Na$_2$S$_2$O$_8$ as initiators, respectively, and isopropyl alcohol (C$_3$H$_7$-OH) was applied as the corresponding CTA. Then, PANs prepared by RAFT polymerization with different molecular weights were termed as R1-R4 (Table 1). The RAFT CTA used in this work is 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid (C$_{12}$H$_{25}$-CTA) (Figure S1).
Scheme 1. Polymerization of AN through various methods with different initiators and CTAs. a)-d) FRP; e) RAFT.

2.2 Characterization of PANs

To confirm the structures of synthesized polymers, NMR and FTIR spectroscopic characterization were performed. Figures 1a and 1b show the $^1$H NMR spectra of F1-F4 and R1-R4, respectively. The peaks at around 3.13-3.08 and 2.11-2.00 ppm correspond to the backbone methine (CH) protons and methylene (CH$_2$) protons, respectively. The NMR results of synthesized PANs are in agreement with that of the commercial product.$^8$ Figure 1c and Figure S2 show the IR spectra of different PAN samples, in which the absorbance peaks at 2240 and 1450 cm$^{-1}$ belong to C≡N stretching and C-H vibration of PAN.$^{27, 28}$ In addition, the number average molecular weights ($M_n$) of PANs were examined by GPC (Figure S3), and the corresponding values of $M_n$ and dispersity are shown in Table 1.

Figure 1. $^1$H NMR spectra of F1-F4 (a) and R1-R4 (b), and IR spectra of F1-F4 and R1.
Table 1. Reaction conditions and reagents used for the polymerization of different PAN samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PANs</th>
<th>Initiator</th>
<th>CTA</th>
<th>Solvent</th>
<th>$M_n^a$ (kg/mol)</th>
<th>$D^a$</th>
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<tr>
<td>1</td>
<td>F1</td>
<td>AIBN</td>
<td>/</td>
<td>DMF</td>
<td>333.1</td>
<td>1.75</td>
</tr>
<tr>
<td>2</td>
<td>F2</td>
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<td>$C_{12}H_{25}$-SH</td>
<td>DMF</td>
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<tr>
<td>3</td>
<td>F3</td>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>$C_3H_7$-OH</td>
<td>DMF</td>
<td>95.0</td>
<td>1.54</td>
</tr>
<tr>
<td>4</td>
<td>F4</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>$C_3H_7$-OH</td>
<td>DMF</td>
<td>158.5</td>
<td>1.65</td>
</tr>
<tr>
<td>5</td>
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<td>AIBN</td>
<td>$C_{12}H_{25}$-CTA</td>
<td>DMF</td>
<td>117.3</td>
<td>1.51</td>
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<tr>
<td>6</td>
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<td>AIBN</td>
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<tr>
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<td>DMF</td>
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<td>1.14</td>
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</table>

$^a$ Measured by GPC in DMF by using PMMA as standards.

2.3 Photophysical properties of PANs

As reported by previous studies, blue emission can be observed in the concentrated solutions and solid powders of PAN, due to the clustering of cyano groups and rigid conformations.$^8,^9$ For the PANs synthesized in this study, we see distinct differences of their daylight emission as well as their PL when irradiated under 365-nm UV light from a handheld UV lamp. As shown in Figure 2, the white powders of F1 and F2 exhibited sky-blue light emission under 365-nm UV light. Impressively, we observe that the brownish powders of F3 and F4 have bright green emission under 365-nm UV light. Moreover, the daylight yellowish powder of R1 shows yellow emission. These observations suggest that the luminescent properties of PANs are quite distinct when utilizing different radical polymerization methods.
Figure 2. Photographs of solid powders for F1-F4, and R1 taken under daylight and 365-nm UV light.

Figures 3a and 3b show the UV-vis absorption spectra of PANs prepared by different radical polymerization methods in both, DMF solution and solid states, respectively. For all PANs, no obvious peak was observed above 350 nm, confirming the non-conjugated nature of these structures. For F1 and F2, their emission wavelengths are around 400 nm in solution, whereas the emission wavelengths red-shifted slightly to 409 nm and 404 nm in the solid films (Figures 3c and 3d). It is found that both F1 and F2 in solution show obvious excitation-dependent emission (Figures S4 and S5, and Table S1). It can be seen from Figure S4 that F1 emits in a wide range of excitation wavelengths. When the concentration of DMF solution of F1 is 5.3 mg/mL, we see emission under 315-395 nm excitation. The optimal excitation wavelength is 345 nm, and the optimal emission peak is at 403 nm. When increasing the concentration of F1 to 53 mg/mL in DMF, we find emission for 315-405 nm excitation with optimal excitation wavelength of 355 nm and emission peak at 407 nm. When the concentration of F1 further is increased to 106 mg/mL in DMF, we see emission for excitation at 315-435 nm, and the optimal excitation wavelength is 365 nm with optimum emission peak at 425 nm wavelength.

Looking at these results, we can state that with increasing concentration of F1 in DMF the range of its excitation wavelengths becomes wider, and the optimal excitation wavelength red-shifts. Likewise, the emission of F3 exhibits a strong dependence of the excitation wavelength on its concentration in DMF solution (Figure S6). It is found that two emission peaks can be observed at 400 and 500 nm, respectively, when F3 was
excited by UV light with wavelength shorter than 400 nm. According to the CTE mechanism\(^1\),\(^10\), the luminescence of PAN originates from cyano group clusters. Therefore, as the PAN concentration increases, more clusters with different intrinsic structural features are generated, resulting in the widening of the excitation wavelength range. Finally, we have investigated lifetimes and PL quantum yield (QY) of PANs in solution with different concentrations, too, and found that the lifetimes and PLQYs are almost independent with the concentration (Table S1).

Figure 3. Normalized UV-vis (a) and PL spectra (c) of F1-F4 in DMF solution (5 mg/mL), and normalized UV-vis (b) and PL spectra (d) of the solid films of F1-F4. Excitation wavelength: F1 and F2 solutions: 340 nm; F1 and F2 solid films: 330 nm; F3 and F4 solutions: 440 nm; F3 and F4 solid films: 445 nm.

For the polymerization of F1 and F2 we have utilized very straightforward synthesis conditions, and besides acrylonitrile, the only additives are AIBN and C\(_{12}\)H\(_{25}\)-SH, which doesn’t interfere with the intrinsic emission of PAN.\(^8\),\(^30\)-\(^32\) Interestingly, PANs synthesized by using persulfate salts as initiators, \(i.e.,\) F3 and F4, exhibited distinct different photophysical properties compared to PAN synthesized with AIBN as initiator. In DMF solution, the absorption peaks of F3 and F4 appeared at 350 nm, 441 nm and 471 nm, respectively (Figure 3a), whereas in solid films, two broad absorption peaks at 350 nm and 458 nm are observed for both F3 and F4 (Figure 3b). In solution
as well as in the solid state, the emission peaks of F3 and F4 are around 505 nm for excitation at 440 nm (Figures 3c and 3d), which is consistent with the color appearance of the powder samples in Figure 2. Further, as discussed earlier, the emission of PAN is strongly influenced by the excitation wavelength used, which is the case for samples F3 and F4, too. For example, exciting F3 solution at 590 nm results in red-shifted emission at 636 nm wavelength (Figure S6c). These results indicate that the application of persulfate initiator significantly changes the intrinsic PL properties of PAN. Such a strong bathochromic shift is rarely observed for the reported NCLPs.\textsuperscript{30-32}

We speculate that the large red-shift of the PAN emission is caused by small changes of their chemical structures. We have performed a number of experiments to eventually find evidence for such small chemical modifications. First, we excluded that the red-shifted emission of F3 and F4 is attributed to oxidation of PAN in the presence of peroxysulphates (see details in SI, Figure S7). Further, it is reported that hydrolysis of PAN may take place at alkaline environment, leading to the formation of conjugated sequences of C=N bonds.\textsuperscript{33-37} To address this potential influence of hydrolysis on the emission of PAN, F1 was dissolved in DMF and heated with NaOH at 70 °C for 300 min (termed as F1-NaOH). Interestingly, an intense absorbance peak appears at around 400 nm in both, the solution and solid film samples of F1-NaOH and the emission peaks of F1-NaOH in solution and solid films are 490 nm and 505 nm, respectively, which are close to those of F3 and F4 (Figure S8).

To further address the emission mechanism of F3 and F4, we prepared a series of PANs by using AIBN as initiator in the presence of NaOH. The molar ratios of NaOH/AN were 1/4000, 1/2000, 1/1000, 1/500, 1/200, 1/100, and 50/1 (termed as F5-F11). It is found that with increasing NaOH concentration, the absorption bands of PANs at 400 nm are gradually enhanced in both the solution and the solid state. Also, the emission spectra of PANs red-shifted with increased NaOH concentration (Figure S9). In particular, in the presence of small traces of alkaline compounds (less than 0.03% on a molar basis), the intrinsic emission of PAN alters significantly. These results suggest that the intrinsic emission of F3 and F4 is due to the presence of traces of
alkaline impurities in the persulfate initiators, resulting in the formation of conjugated segments.

Figure 4a shows a possible formation mechanism of conjugated structures in PAN synthesized in the presence of traces of alkaline impurities. In the presence of OH⁻ groups, alkaline hydrolysis reaction would occur during polymerization, leading to the formation of conjugated segments with C=N bonds. To verify our speculation, synthesized PANs were investigated by X-ray photoelectron spectroscopy (XPS). Figure S10 shows the XPS spectra of F3, however, the signal related to C=N bond was not observed. Also, no C=N peaks can be observed in the XPS spectra of F11 (Figure S11), the PAN with highest NaOH/AN ratio. It may be due to the low concentration of conjugated segments.

Figure 4. (a) Hydrolysis mechanism of PAN under alkaline conditions. (b) Molecular orbital energies of conjugated structures in hydrolyzed PANs.

To gain a deeper insight on the interference of conjugated sequences on the intrinsic emission of PAN, density functional theory (DFT) calculations were performed. Figure 4b shows the energies of the HOMO and LUMO of conjugated structures with different numbers of repeat units, as well as the values of the corresponding energy gaps ($E_g$). With the increasing number of semi-conjugated rings,
the HOMO is increasing from -6.56 to -6.28 eV, while the LUMO decreases from -1.43 eV to -2.49 eV, resulting in a smaller $E_g$ (from 5.13 to 3.79 eV). Therefore, based on the experimental and theoretical results, we conclude that conjugated segments in hydrolyzed PAN are responsible for the red-shift of absorbance and emission spectra.

Besides the simple presence of conjugated segments, in addition the presence of a Föster-type resonance energy transfer (FRET) process may cause changes of the PL properties of F3 and F4, too. The absorbance of PANs synthesized in the presence of NaOH is around 400 nm (Figures S9a and S9b), which is close to the intrinsic emission wavelength of PAN (Figure 3c). In this case, an efficient FRET may occur from luminescent clusters of cyan groups to the conjugated structures. More research on the emission mechanism of PANs synthesized with persulfate initiators needs to be undertaken, and follow-up research is ongoing in our laboratory.

We have investigated the photophysical properties of PANs synthesized by RAFT polymerization, too. As shown in Figure 5a, the absorption peaks of R1 solution in DMF appeared at 320 nm, whereas the absorption spectrum of R1 in the solid film exhibited two peaks at 340 nm and 420 nm, respectively. The absorption peaks of R1 are ascribed to the presence of thiocarbonyl-based CTA end-groups. The emission peaks of R1 in solution and solid films are 433 nm and 477 nm, respectively. We speculate that the red-shift of emission of R1 is ascribed to the presence of thiocarbonyl-based CTA end-groups, too. To justify our assumption, we examined the PL properties of C$_{12}$H$_{25}$-CTA itself. In Figure S12a, it can be seen that C$_{12}$H$_{25}$-CTA clearly has no emission. Moreover, blends of F1 and C$_{12}$H$_{25}$-CTA were prepared by solution mixing (0.5 % and 1 %), and it is found that the intrinsic emission of F1 is preserved in the presence of C$_{12}$H$_{25}$-CTA (Figure S12b).
Figure 5. (a) Normalized absorption and PL spectra of R1 in DMF solutions (5.3 mg/mL) and solid films. Excitation at 378 nm in solution and 365 nm in solid. (b) Normalized PL spectra of R1-R4 in DMF solutions. Excitation at 380 nm (5.3 mg/mL). (c) Dependence of emission wavelength of RAFT-prepared PANs on the molar concentration C_{12}H_{25}-CTA.

However, in the present case the thiocarbonyl-based CTA represents the end-groups of the PAN, i.e., C_{12}H_{25}-CTA is part of the PAN macromolecule, which may cause the change of the intrinsic emission of PAN. To address this hypothesis, we have prepared PANs with different molecular weights (Table 1). As shown in Figures 5b, the emission wavelengths of R1 (117.3 kg/mol), R2 (55.4 kg/mol), R3 (13.6 kg/mol), and R4 (5.6 kg/mol) in solution are 433 nm, 460 nm, 473 nm, and 481 nm, respectively. Therefore, we conclude that the red-shifted emission of PANs is attributed to the increased molar concentration of CTA (ratio of CTA and monomer, f_{CTA}) with decreasing of $M_n$ (Figure 5c). It confirms that the presence of C_{12}H_{25}-CTA end-groups significantly changes the intrinsic PL properties of PAN. These results suggest that the red-shift emission of R1 may be caused by the introduction of thiocarbonyl end-groups into the cyano clusters. Note that, the electron-rich heteroatom sulfur of the thiocarbonyl by itself can form diverse clusters upon aggregation (inset in Figure 5c).^{1} Moreover, sulfur is necessary for the generation of efficient intra- and inter-molecular interactions through the covalent connection of different clustered chromophores.^{32}

As evidenced above, the PL properties of PANs can be tuned by selecting proper radical polymerization routes. Therefore, we can achieve wide-range spectrum emission from single type of polymer. As shown in Figure 6a, ten PANs synthesized by different polymerization methods exhibited PL emission in DMF solution at different wavelengths for certain excitation wavelengths. It gives a wide-range emission covering the range from 400 to 630 nm (Figure 6b). In addition, the PL emission can be further tuned by mixing two or more PANs with different emission wavelengths, both in solution and in solid state. For instance, the emission wavelengths of F1 and F3 are 400 nm and 506 nm (excitation at 345 nm) in DMF solution, respectively. For same
excitation wavelength of 345 nm, in the mixed solution of F1 and F3, two emission peaks can be observed and the initial emission wavelengths of F1 and F3 are almost maintained in the mixtures. The intensity of the two peaks is determined by the weight ratio of F1 and F3, i.e. by simple rule of mixture (Figure 6c). This implies that energy transfer

Figure 6. (a) Normalized PL spectra of PAN solutions with different emission wavelengths under certain excitation, and the corresponding CIE 1931 chromaticity coordinates (b). Normalized PL spectra of F1, F3, and their blends with different weight ratios in DMF solutions (c) and in solid film (e), and the corresponding CIE 1931 chromaticity coordinates (d, f). Excitation at 345 nm.

may not occur in the mixtures between the different PANs. In particular, the F1/F3 blend
(1/4 wt/wt) has a cold-white emission with chromaticity coordinate of (0.26, 0.35) (filled spot in Figure 6d). Moreover, PAN solid state film blends of F1 and F3 have been prepared and show a similar behavior (Figures 6e and 6f). Emission of F1 solid-state sample is detected for 401 nm at 345 nm excitation, which is identical with emission seen in solution. However, F3 solid-state sample shows with 491 nm a substantial lower emission wavelength compared to its solution. We suggest that, in the solid state, the conjugated segments would be separated and frozen by polymer chains, resulting in weakened energy transfer. Anyway, solid-state blend samples follow the same simple rule of mixture, as described above for the solution blending case: two emission peaks are observed, and the intensity of the two peaks again is determined by the weight ratio of F1 and F3 in the solid-state blend. Blending in solution and solid-state provides a possible approach to realize controlled emission patterns of NCLPs.

Conclusions

Utilizing different FRP and RAFT routes for controlled synthesizing PAN, we can tune optical absorbance and PL of NCLPs in a broad wavelength range from 400 nm to 630 nm. All polymers have the typical PAN molecular characteristics as verified by e.g. 1H NMR. The diverse optical properties of the PANs, however, most probably are caused by very small variations of their molecular architecture. Besides common small alterations caused by applying different synthesis routes, we speculate that small traces of the different initiators and CTAs might be incorporated into the macromolecules, too. All together may cause variations of the clustering behavior of the non-conjugated chromophores, which results in PL shifts. For the same reason, the PL emissions of various PANs are dependent on their molecular weights, i.e. concentration of end groups, and the excitation wavelengths.

Because of their almost identical molecular architecture, blending the PANs without causing demixing and unwanted energy transfer is straightforward. We have demonstrated that the PL of blends follows simple rules of mixtures: the blend PL is a superposition of the PL of the blend components, and the PL emission intensity created by each component scales with its concentration in the blend. Blending the PANs
synthesized in this study allows to cover a large area of the color space. Further work is in progress studying the opportunities of blending PANs for simple and controlled tuning of PL emission.

**Experimental Section**

**Materials**

Acrylonitrile (AN) and 2,2'-dipyridyl (bpy) were purchased from TCI, extra dry N,N-dimethylformamide (DMF), extra dry tetrahydrofuran (THF), 1-dodecanethiol, carbon disulfide, 2-bromo-2-methylpropionic acid, 2,2-dimethyl-1,3-propanediol, 1, 4-diaminobutane dihydrochloride, sodium hydroxide (NaOH), ammonium persulfate (\((\text{NH}_4)_2\text{S}_2\text{O}_8\)) , sodium persulfate (Na$_2$S$_2$O$_8$), potassium phosphate, isopropyl alcohol and azobisacetonitrile (AIBN) were purchased from Innochem. After recrystallization, acrylonitrile was purified by neutral alumina column and used.

**Instruments**

Solution $^1$H NMR spectra were measured on a JEOL 500 NMR spectrometer using either DMSO-d$_6$ or chloroform-d as solvent and tetramethylsilane (TMS, $\delta = 0$) as an internal reference. Weight- and number-average molecular weights ($M_w$, $M_n$) and polydispersities ($M_w/M_n$) of the polymers were estimated on a Waters gel permeation chromatography (GPC) system using DMF as eluent. UV absorption spectra were taken on a Shimadzu UV3600PLUS array spectrophotometer. PL spectra were recorded on a Shimadzu RF6000 spectrofluorometer. The fluorescence quantum yields ($\Phi_F$) were measured by using Otsuka Electronics QE-2100. The fluorescence lifetime results were taken from Edinburgh Instruments FLS-980. IR spectra were recorded on a PerkinElmer 16 PC FTIR spectrophotometer. WAXS measurements were executed by Rigaku Nanopix-SP with an ultrahigh-intensity microfocus rotating anode X-ray generator at wavelength of 0.154 nm.

**Synthesis**

All the polymerization reactions were carried out under nitrogen, using the standard
Schlenk technique. The detailed procedures for the preparation of C_{12}H_{25}-CTA, C_{13}H_{22}Br_{2}O_{4}, and PANs are described in the Supporting Information.

**Conflict of Interest**

The authors declare no conflict of interest.

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