POROUS COVALENT ORGANIC POLYMERS USED IN LUMINESCENCE ANALYSIS METHOD

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ПОРИСТЫЕ КОВАЛЕНТНЫЕ ОРАГНИЧЕСКИЕ ПОЛИМЕРЫ, ИСПОЛЬЗУЕМЫЕ В ЛЮМИНИСЦЕНТНЫХ МЕТОДАХ АНАЛИЗА

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Аннотация. *В последнее время химическая промышленность развивается колоссальными темпами, вследствие чего активно растёт объём применяемых химических продуктов, которые в свою очередь приводят к загрязнению почвы, водных биологических систем и окружающей среды. Для контроля качества окружающей среды используются различные методы анализа, мы решили рассмотреть один из наиболее быстрых и чувствительных методов, люминесцентный. Поэтому мы решили получить пять различных образцов пористых ковалентных веществ, которые могут быть использованы, как анализаторы при люминесцентном методе.*

Introduction. Nowadays the luminescent method of research, characterized by high sensitivity and speed, so it is more widely used in the veterinary-sanitary inspection and epidemiological surveillance.

The luminescent method of analysis covers a wide range of methods for the determination of various objects from simple ions and molecules to macromolecular compounds and biological objects. The object or its derivatives are detected by luminescence.

The quantitative luminescent analysis is based on the dependence between the luminescence intensity and the concentration of the luminescent substance. At low concentrations of the substance in the solution luminescence intensity is proportional to its content. At high concentrations of luminescent substance, violation of the proportions is observed. Quantitative fluorescence analysis technique includes the empirical determination of the relationship between the concentration of the test substance and the intensity of luminescence. The same dependence for a series of standard solutions with the given amount of analyzed substance has to be preset. According to the data obtained from measuring a series of standard solutions, the calibration curve is obtained. Whereby the sample solution on the luminescent emission intensity determining concentration of the substance therein. A number of methods of quantitative fluorescence analysis don't use a pre-defined calibration schedule, but the luminescence intensity of a standard solution is determined through the analysis.

The advantage of the methods of luminescent analysis is a very high sensitivity. Thus, a fluorescein dye can be detected by its luminescence when its concentration in the solution is about 10^{-8} mol / liter, and the absorption of light with a spectrophotometer occurs only at the concentrations of 10^{-5}–10^{-6} mol / liter. By measuring the intensity of the luminescence solution with the given concentration of the substance, it is possible to determine the concentration of the substance in the test solutions. Another advantage of luminescent methods of analysis is that they are more tangible when working with multicomponent media, if analyzed substance or at least a region of the spectrum luminesces (it can be identified by means of optical filters), in which it mainly luminesces. For this purpose, photovoltaic fluorometers are used.

Luminescent techniques are divided into two groups:

1. The techniques based on their own observation of the luminescence of the analyzed substance (varietal analysis);

2. The techniques based on the observation or occurrence of luminescence quenching by the interaction of the analyzed substance with a reagent (fluorescent chemical analysis).

Between the two groups of analysis - varietal and chemical there is no sharp boundary, as the chemical luminescence analysis, when used as a rapid method, to a large extent becomes varietal and vice versa.

As the source of ultraviolet rays a special incandescent lamp or a discharge lamp is used.

Experimental material and procedure. The following results were derived from Lin Guo & Dapeng Cao [2]. The covalent–organic materials (COM) become better candidates as luminescent probes owing to their rich extended systems and high hydrothermal stability. A series of conjugated microporous polymer materials (CMP) have been synthesized and can be used as luminescent probes for the detection of reactive NO_x gases and oxidative ions.

Here, by tuning the ratios of two monomers of 1,3,6,8-tetrabromopyrene (TBP) and 1,3,5-tris-(4-bromophenyl) benzene (TBB), a series of porous covalent–organic polymers (COPs) is synthesized by using the Ni-catalyzed Yamamoto reaction. The resulting COP materials exhibit strong luminescence with wide emission peaks ranging from 533 up to 815 nm, also color tailoring can be achieved. Moreover, these porous COPs also exhibit high sensitivity and selectivity for sensing of nitroaromatic explosives and metal ions.

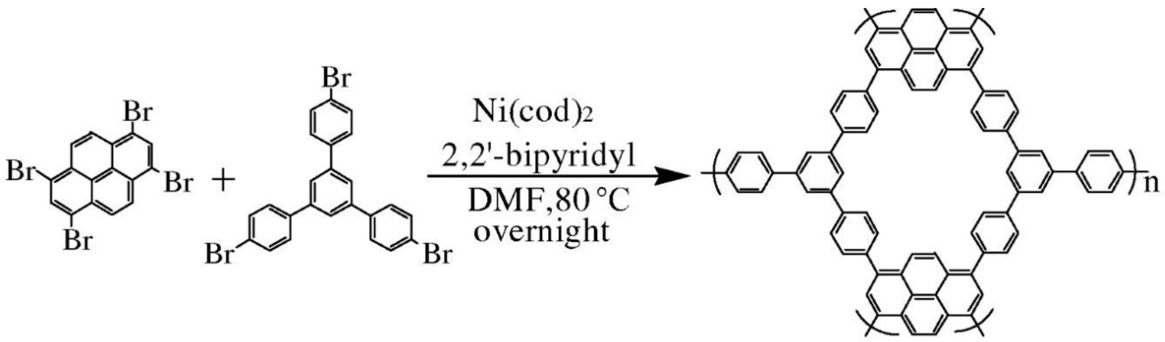

Fig. 1. Synthetic route to the COPs by using 1,3,6,8-tetrabromo pyrene (TBSP) and 1,3,5-tris(4-bromophenyl)benzene (TBB) as double monomers via the nickel-catalyzed Yamamoto-type

The synthetic scheme of the COPs is shown in Fig. 1 The five COP samples were synthesized in five different monomer ratios 2 : 3, 1 : 1, 3 : 2, 4 : 1 and 9 : 1 by using the Ni-catalyzed Yamamoto reaction.

For convenience, the five COPs are marked as COP-61, COP-62, COP-63, COP-64 and COP-65, respectively.

The solid-state photoluminescence (PL) spectra of the five COPs at room temperature are shown in Fig. 2 and the detailed excitation. Compared to TBB (the luminescence intensity of TBB is very weak and only 72), the luminescence intensity of the five COPs exhibits an increase of several orders of magnitude (in particular, COP-61 reaches 5500). Moreover, the emission peaks of the five COPs show a significant red-shift. The observation above may be attributed to the formation of extended π conjugation in the COPs. As shown in (Fig. 2), COP-61, COP-62 and COP-63 show a single emission peak of 533, 543 and 555 nm when excited at 344 nm, whereas COP-64 presents a broad peak located at 655 nm upon excitation at 469 nm. Interestingly, COP-65 shows a broad emission peak at 815 nm when excited at 532 nm, which is much longer than the emission peaks of all previously reported porous organic materials.

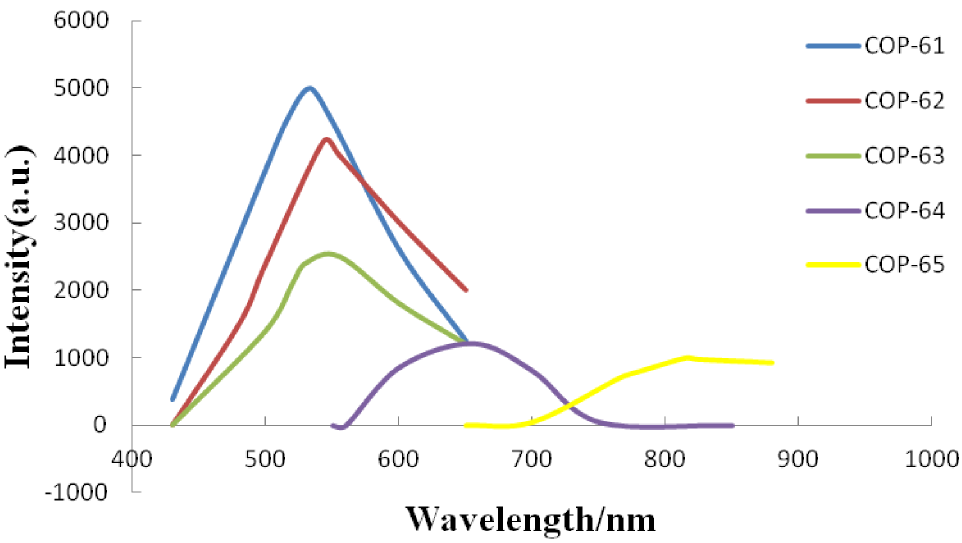

Fig. 2. PL spectra of the five solid COP materials

All the five COPs show strong solid state fluorescence with wide emitting colors ranging from yellow-green (COP-61), to light yellow green (COP-62), yellow (COP-63), orange (COP-64) and red (COP-65).

Conclusion. A series of porous covalent organic polymers (COPs) were synthesized using the Ni-catalyzed Yamamoto reaction. By adjusting the reactive ratios of two monomers, color diversity of the resultant COP samples was successfully achieved. Interestingly, the emission peaks of these porous COP samples cover a wide color range from 533 up to 815 nm. Further study indicates that these porous COPs can serve as luminescent sensors for highly sensitive and selective sensing of nitroaromatic explosives and metal ions. These materials might also find more applications in photocatalysis, organic electronics and medical imaging.

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