# Iodinated molecularly imprinted polymer for room temperature phosphorescence optosensing of fluoranthene

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**A novel molecularly imprinted polymer (MIP) of high interest for room temperature phosphorescence (RTP) sensing systems is described; the synthesized MIP contains iodine as internal heavy atom in the polymeric structure and its applicability for RTP sensing of fluoranthene at μg L$^{-1}$ levels is demonstrated.**

Polycyclic aromatic hydrocarbons (PAHs) are well-known hazardous chemicals with carcinogenic and mutagenic character, originated from incomplete combustion of organic matter. In line with this, the European Parliament and the Council of the European Union have included fluoranthene (as an indicator of other more dangerous PAHs) in a list of 33 priority substances in the field of water policy.[1]

Identification and quantification of PAHs are usually performed by means of liquid and gas chromatography. On the other hand, PAHs' native luminescent properties have been exploited in the design of sensors for *in-situ* analysis and several optosensors for PAHs control have been described so far, with different degrees of success, based on on-line pre-concentration of the analytes onto different solid supports.[2–8] In recent years, molecular imprinting techniques have turned out to be an attractive tool to enhance the sensitivity and selectivity of luminescence optosensors through the development of robust tailor-made molecularly imprinted polymers (MIPs) as active phases for recognition.

Recently, some approaches for the development of MIPs-based fluorescent sensing systems have been described.[9–14] However, no organic MIPs-based room temperature phosphorescence (RTP) sensing systems have been reported to date, even though phosphorescent detection provides a series of important advantages, including wide separation between the excitation and emission spectra as well as low background emission. Besides, since phosphorescence is less common than fluorescence the selectivity of the detection is highly increased. In addition, interferences from any short-lived fluorescence and scattered light can be easily avoided using an appropriate delay time.

One pending topic related to the synthesis of MIPs is the undesirable formation of unspecific cavities, leading to non-specific recognition.[15] Moreover, undesirable non-specific adsorption may occur on a polymer surface depending on the hydrophobicity of the MIP surface and the presence of monomer residues randomly distributed to the surface. With the aim of increasing specificity for sensing purposes, here we investigated the possibility of combining the important advantages of MIPs with those provided by phosphorescent detection. In order to achieve RTP analytical signals, an adequate heavy atom (*e.g.* Br, I, Tl) must be present to populate the excited triplet state of the phosphor by increasing the rate of intersystem crossing.[16] In many cases, the heavy atom is added to the samples using a high concentration of salt in aqueous solution. However, such methodology lacks general use and has some inconveniences, including impurities in the reagents, cost of the heavy atom salts, *etc.*[17] In this work, we have investigated the use of an iodinated monomer in the polymerization (so ensuring that the heavy atom is already present in the polymeric structure of the MIP). The potential applicability of this novel iodinated polymer for RTP fluoranthene optosensing has been evaluated and compared to that of the corresponding traditional non-iodinated polymer.

The iodination of bisphenol A to obtain the monomer tetraiodobisphenol A (4,4′-isopropylidenedi(2,6-diiodophenol)) was carried out using $IPy_2BF_4$ (bis(pyridine)iodinium(I) tetrafluoroborate) as iodinating agent†.[18]

Then, an iodinated polyurethane was prepared through bulk polymerization at room temperature starting from fluoranthene (as the template molecule), tetraiodobisphenol A and diphenylmethane-4,4′-diisocyanate (MDI) as functional monomers, phloroglucinol as an additional cross-linker and tetrahydrofuran as solvent‡ (see Fig. 1)§. Control (non-imprinted) polymer was prepared and treated in exactly the same way, except that no print molecule was used in the polymerization stage.

The analogous non-iodinated polyurethane MIP was prepared exactly as the iodinated polymer, except that tetraiodobisphenol A was replaced by the appropriate equimolar amount of bisphenol A.

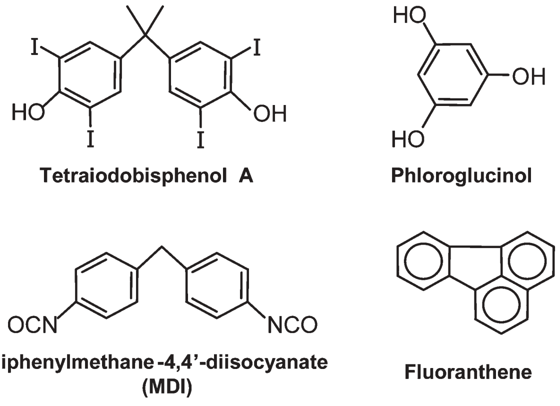

**Fig. 1** Chemical structures of the selected template and monomers for the synthesis of the iodinated molecularly imprinted polymer.

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The performance of the non-iodinated MIP was initially tested. First, the template molecule (fluoranthene) was removed from the polymer by passing a continuous flow of acetonitrile until the template in the extraction solvent could not be detected by fluorescence. Then, the washed polymer was packed in a conventional luminescence flow-through quartz cell and this flow-cell was placed inside the sample holder of a Varian Cary Eclipse luminescence spectrometer. Since molecular oxygen is a very efficient quencher of phosphorescence, it was removed from the samples by its reaction with sodium sulfite.[19] Thus, fluoranthene aqueous solutions containing 2% of acetonitrile, KI as an external heavy atom and $Na_2SO_3$ as oxygen scavenger were pumped through the polymer using a peristaltic pump (see Fig. 2) at a constant flow rate of 1 mL $min^{-1}$. Although fluorescence emission from fluoranthene retained in the MIP could be observed, no RTP emission was detected when working with the non-iodinated polymer.

Then, the iodinated MIP was thoroughly tested. The polymer was packed in the flow cell and its RTP emission spectrum, while passing a distilled water flow through the flow cell, was recorded. Two very intense fluoranthene phosphorescence emission peaks (at 550 and 593 nm) were observed, even in the absence of a deoxygenating agent (see Fig. 3). This fact suggests that fluoranthene imprinting molecules rest within such a rigid environment that their phosphorescence emission is protected even from dissolved oxygen quenching effects.

The tight confinement of the template molecules within the polymer structure was responsible for the need for an aggressive treatment to accomplish the polymer washing step. In fact, the difficulty of completely removing the template molecule from MIPs is a well known issue in molecular imprinting.[20] The imprinting molecule was removed by means of microwave-assisted extraction¶. Afterwards, the MIP phosphorescence emission at 550 nm was checked once again. As can be seen in Fig. 3, as a result of the microwave treatment the fluoranthene imprinting molecule was almost completely removed from the polymer, since the observed phosphorescence emission due to residual fluoranthene molecules can be considered negligible.

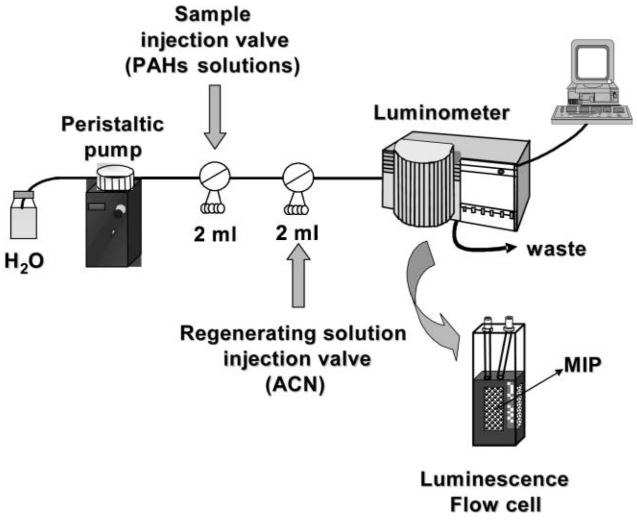

**Fig. 2** Optosensing manifold for RTP monitoring of fluoranthene after its retention by the imprinted polymer.

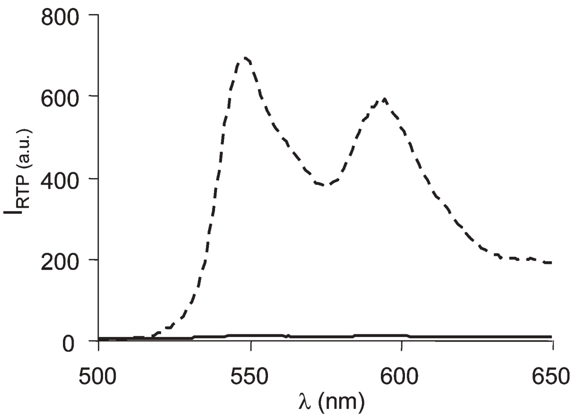

**Fig. 3** RTP emission spectrum ($\lambda_{ex}$ = 365 nm) of fluoranthene (template molecule) in the iodinated imprinted polymer (dashed line). RTP spectrum of the polymer after template removal *via* a microwave treatment (solid line).

To verify whether this iodinated polymer retained recognition properties after the microwave treatment and to evaluate its potential as sensing material, a fluoranthene solution (10 μg $L^{-1}$) was prepared and pumped through the packed MIP (see Fig. 2). As expected, after the microwave-assisted template extraction, subsequent fluoranthene rebindings seemed to be weaker, since deoxygenation of the samples with sodium sulfite was necessary in order to achieve a detectable fluoranthene RTP emission. Fig. 4 shows the response profile of the MIP for three successive injections of the fluoranthene aqueous samples (2 mL sample). Now, the removal of the retained fluoranthene after each injection is straightforward and can be accomplished by a 2 mL acetonitrile flow (thus proving that the MIP can be easily regenerated).

In order to verify that the observed RTP emissions derive from fluoranthene retained in the MIP selective cavities, rather than from simple adsorptions on the material, the RTP emission from a 20 μg $L^{-1}$ fluoranthene aqueous solution injected through the MIP was compared to that obtained after injecting the same

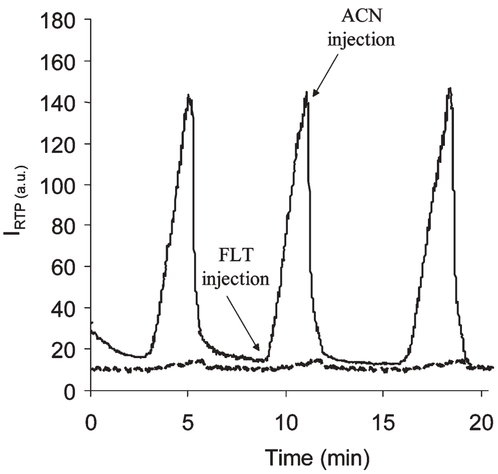

**Fig. 4** RTP response profile ($\lambda_{ex}$ = 365 nm, $\lambda_{em}$ = 550 nm) of the iodinated MIP (solid line) and the non-imprinted polymer (NIP, dashed line) for three successive fluoranthene aqueous samples injection (10 μg $L^{-1}$). For polymer regeneration, acetonitrile (ACN) is injected after each sample injection.

fluoranthene solution through the control (non imprinted) polymer similarly packed in the flow-cell. The RTP signal obtained from the control polymer was negligible. We have also carried out fluoranthene retention studies in the NIP, using fluorescence detection, showing that fluorescent fluoranthene molecules are partially retained on the NIP surface. However, since phosphorescence is a luminescence phenomenon typical of molecules in a "highly rigid" environment (tailor-made cavities of MIPs in our particular case), any simple adsorption process does not ensure enough rigidity to produce RTP emissions. Moreover, a "heavy atom effect" by the iodine atoms is also needed. Therefore we can assume that the RTP recognition results from host–guest interactions between the iodinated MIP cavity matrix and the target molecule.

Finally, a selectivity study showed that the combination of the RTP detection with the recognition by the iodinated MIP is highly selective to the fluoranthene molecule when exposed to mixtures of this compound (10 μg $L^{-1}$) and other PAHs (*e.g.* 40 μg $L^{-1}$ of naphthalene, benzo(*a*)pyrene and benzo(*b*)fluoranthene). In summary, molecular imprinting using a novel iodinated monomer, tetraiodobisphenol A, for copolymerization with MDI, is proposed here for chemical recognition of photoluminescent analytes by means of RTP detection. The occurrence of a "heavy atom effect" when the imprinted polymer contains iodine in its structure has been shown to be responsible for inducing the highly intense RTP emission observed. Thus, this novel iodinated MIP has shown a great potential for the development of selective and simple and easy to use RTP optosensors, opening new paths for the development of high performance MIP-RTP optosensors for different applications.

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## Notes and references

† Bisphenol A (5 g, 21.90 mmol) was suspended in dichloromethane (200 mL), iodination reagent $IPy_2BF_4$ (33.48 g, 90 mmol) was added and the mixture was stirred at room temperature overnight. Distilled water and HCl (1%) were added up to acid pH. The organic phase was separated and washed with water (3 × 100 mL), thiosulfate (5%, 100 mL) and again water (2 × 100 mL) and then was dried over $Na_2SO_4$. Finally, the organic solvent was removed by rotary evaporation and the crude solid was washed with ether (2 × 10 mL) to give a pure product in 85% yield. Spectral data ($^1$H and $^{13}$C) were in full agreement with the assigned structure.

‡ Fluoranthene (20 mg), phloroglucinol (70 mg) and tetraiodobisphenol A (612 mg) were placed in a glass vial and 5 mL of an MDI solution (70 mM) in THF were added. The mixture was stirred and stored uncapped in the absence of light for 4 days until complete evaporation of the organic solvent. The solid obtained was ground in an agate mortar, washed with acetonitrile (3 × 5 mL) and dried at 30–35 °C. The ground polymer was sieved and particle sizes of diameters between 80 and 160 μm were selected.

§ **CAUTION** Special caution was taken in the handling of fluoranthene and in the preparation of the MIPs. Nitrile globes, protective clothing and safety glasses were worn all the time. A respirator equipped with two organic vapour/particulate filters was used. Hazardous wastes were collected, stored in glass containers, labeled and sent to a waste management company.

¶ 100 mg of the polymer were placed in a PTFE vessel and 4 mL of a MeOH/hexane (1 : 1) mixture were added. The vessel was tightly capped, placed in the microwave oven and treated at 30 W for 5 minutes. Then the polymer was finally cleaned with ethanol and left to dry at room temperature.

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