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# Preparation and photochemical properties of *p*-phenylene oligomers encapsulated within faujasite Y

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**Phenylene oligomers have been prepared by ship-in-a-bottle synthesis inside palladium containing basic zeolites by homocoupling of 1,4-phenylenediboronic acid. Product analysis and "*in situ*" IR spectroscopy support the formation of oligomers of three to five phenylene rings. The encapsulated oligomers emit the characteristic blue light upon excitation and laser flash photolysis reveals the formation of long-lived transient decaying in hundreds of μs that has been attributed to the corresponding triplet excited state.**

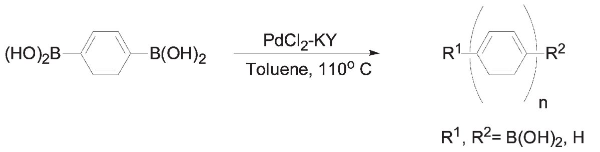
## Introduction

Encapsulation of organic compounds inside the rigid pores of zeolites has become a routine tool in supramolecular chemistry to alter and control the photophysical properties of incarcerated guest.[1] Particularly challenging is when the organic guest is too large to be adsorbed from the exterior into the internal pores. In this case, ship-in-a-bottle methodologies have to be devised to achieve the *in situ* synthesis of the target guest. This is the case of organic polymers or oligomers encapsulated inside zeolites. Polyphenylene oligomers can exhibit intense electroluminescence[2,3] and it would be of interest to study their properties when encapsulated within zeolites. Concerning the emission efficiency it had been demonstrated that the conformational mobility of the phenylene rings permitting the ring twisting is one of the major radiationless deactivation pathways causing the decrease of emission quantum yields. To overcome this limitation a strategy has consisted in the chemical modification of the polymers by putting methylene bridges between two consecutive phenylene rings (polyfluorene derivatives) that thwart the mobility of the rings.

An alternative to the modification of the phenylene by substitution that would require more elaborated starting materials would be its incorporation inside the rigid framework of microporous hosts. As a general phenomenon it has been observed that incorporation of a guest inside the zeolite micropores disfavors radiationless deactivation pathways arising from conformational mobility.[1] Herein, we describe the *in situ* synthesis of *p*-phenylene oligomers (PP) inside the cavities of faujasite-Y and the photochemical properties of the resulting encapsulated oligomers.

## Results and discussion

In order to effect the *p*-phenylene coupling one of the current most versatile reactions consists in the Suzuki–Miyaura homocoupling of 1,4-phenylenediboronic acid in toluene using Pd-complexes as catalysts in basic media.[4,5] Recently we have supported palladium species on zeolites and used the resulting solids as heterogeneous catalysts for the Suzuki–Miyaura cross coupling.[6] Moreover, by using basic zeolites we have demonstrated that the Suzuki–Miyaura reaction catalysed by zeolites supporting palladium salts does not require the presence of extrinsic base.[6] In particular, potassium exchanged Y zeolite (KY) was found to exhibit an adequate basic strength for the reaction of bromobenzene and phenylboronic acid.[6] In view of the activity of these zeolites to effect the Suzuki–Miyaura reaction it occurred to us that it should be possible to apply this strategy to effect the ship-in-a-bottle synthesis of phenylene oligomers entrapped inside the zeolite cavities.



(1)

Eqn. (1) shows the reaction employed for the synthesis of *p*-phenylene oligomers. The reaction was carried out in toluene at 110° and its progress was monitored by observing in the liquid phase the formation of terphenylene and *p*-tetraphenylene derivatives. We expected that the same type of compounds were also formed within the interior of the pores and that due to the linear geometry and rigidity of these compounds, the diffusion through the pores will be impeded. If this were the case then a certain amount of oligomers formed in the zeolite cavities would become imprisoned inside the pores without any possibility to diffuse to the exterior of the particle. To support this likely possibility, a sample of KY zeolite after being used for the reaction of 1,4-phenylenediboronic acid was dissolved using concentrated HF acid and the resulting liquor extracted with dichloromethane in order to recover the organic material adsorbed within the pores. This extract was analysed by CG-MS, FAB-MS and $^1$H-NMR.

The GC-MS after dissolving the solid reveals a complex mixture, mostly being terphenylene (80%) accompanied with tetraphenylene (10%) and other oligomers. Deboronation catalyzed by Pd occurs concomitantly with the Suzuki homocoupling. In the FAB-MS of the liquor after dissolving the zeolite, peaks corresponding to up to 5 aromatic rings (detected in the GC-MS) were observed. $^1$H-NMR of the organic extract after dissolving the $PdCl_2$–KY also shows the presence of aromatic protons appearing as unresolved peaks between 7.8 and

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7.2 ppm. The presence of a residual amount of acid protons of the boronic acid groups was also assessed by a signal around 9.0 ppm.

Concerning the size of the oligomers product analysis suggests a distribution of short oligomers of 3, 4 and 5 rings with an approximate distribution of 70, 15 and 5%, respectively. Taking into account the rigidity of the polyphenylene oligomers, its linear geometry as well as the geometry of the faujasite micropores formed by cavities tetrahedrally arranged, the most likely possibility is that the phenylene oligomers occupy two neighbour cavities (around 26 Å length). Molecular modelling using the optimized geometry for zeolite and phenylene oligomers indicates that the maximum number of polyphenylene units that can be accommodated inside the zeolite cavities corresponds to 5. This prediction would be compatible with the product distribution observed upon dissolving the solid with HF in which the maximum number of rings observed was 5.

Spectroscopic characterisation of the PP-loaded $PdCl_2$–KY zeolite is also compatible with the presence of phenylene oligomers. In particular, FT-IR spectroscopy of the PP loaded zeolite after outgassing at 300 °C to remove co-adsorbed water and volatile solvents also shows the presence of aromatic rings as indicated by the characteristic vibration bands appearing from 1700 to 1500 $cm^{-1}$. Fig. 1 shows the aromatic region of the PP loaded $PdCl_2$–KY compared to the IR of an authentic sample of PP prepared by conventional synthetic procedures using $Pd_2(dba)_3$ as catalyst under the reaction conditions analogous to those used for the preparation of the zeolite encapsulated oligomers.

Diffuse-reflectance UV-Vis spectroscopy of the zeolite after the Suzuki–Miyaura coupling also reveals the presence of aromatic compounds adsorbed in the solid exhibiting as the most intense absorption band at 260 nm together with other less intense bands around 350 nm.

The PP loaded $PdCl_2$–KY exhibits the characteristic PP photoluminescence peaking at 465 nm when the sample is excited at 380 nm. Fig. 2 shows the corresponding emission and excitation spectra recorded for the zeolite encapsulated PP. While the maximum at 480 nm and the corresponding shoulders are due to the PP emission, the peak at 620 nm corresponds to an optical artefact due to the front-face arrangement used to measure the emission in opaque powders. Oxygen purging does not noticeably decrease the emission intensity and, therefore, the encapsulated PP is a fluorescent solid in the open air. According to the data reported in the literature[7] the emission and excitation spectra shown in Fig. 2 is very similar to that of pure PP, although the emission of encapsulated PP is somewhat broader and less vibrationally resolved than that observed for pure PP thin films. However, it has to be noted that according to the literature the photoluminescence of pure PP becomes broader when the emission is recorded for powders rather than for films.[7]

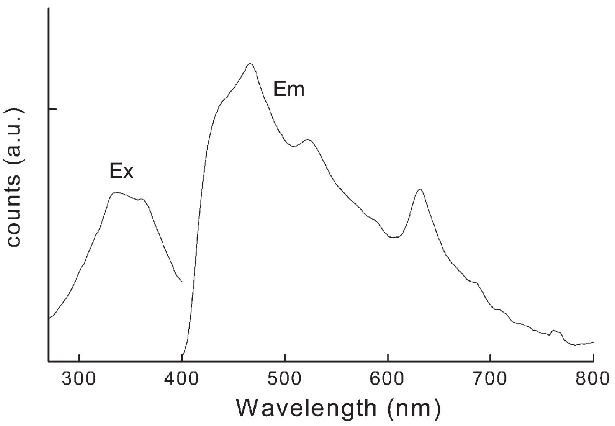

**Fig. 2** Emission ($\lambda_{ex}$ 380 nm) and excitation ($\lambda_{em}$ 465 nm) spectra of PP incorporated within $PdCl_2$–KY.

The sample of PP encapsulated in zeolite was submitted to laser flash photolysis. This photochemical technique is complementary to photoluminescence studies, allowing the detection of photochemical generated transient species even if they are not emissive. Upon 266 nm laser excitation a diffuse reflectance absorption spectrum decaying in the μs time-scale was recorded (Fig. 3). Analysis of the signal temporal profile at different wavelengths (inset of Fig. 3) shows that the decays are coincident suggesting that the transient spectrum corresponds to a single species.

Given the experimental difficulty in performing quenching studies in solid samples, the nature of the transient generated upon laser flash photolysis on zeolites is generally addressed by comparing the optical spectrum recorded in zeolites with those obtained for the same compound in solution.[1,8] Much to our surprise a search through the chemical database reveals that the laser flash photolysis study of PPP has never been previously reported. Therefore, in order to address the nature

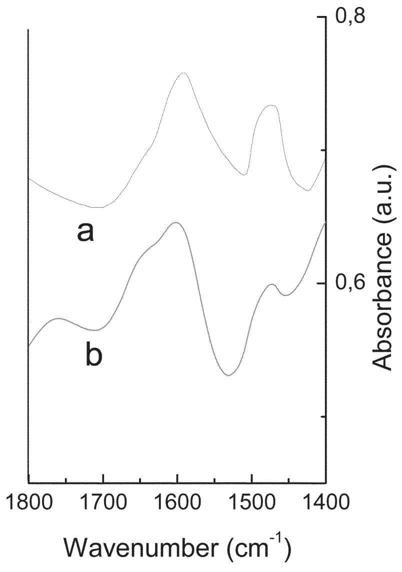

**Fig. 1** IR spectra of the PP recorded at room temperature in KBr (a) and PP loaded $PdCl_2$–KY recorded after outgassing at 300 °C at $10^{-2}$ Pa (b).

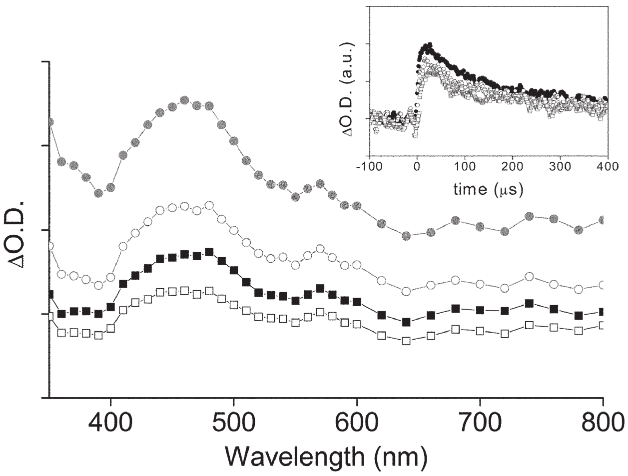

**Fig. 3** Diffuse-reflectance UV-Vis transient spectra recorded for nitrogen purged PP incorporated within KY after 266 nm laser excitation. The spectra have been recorded at 35 (●), 100 (○), 160 (■) and 235 (□) μs delay. The inset shows the signal decay monitored at 460 (●), 570 (○) and 6850 (□) nm, indicating that the whole spectrum corresponds to a singlet transient.

of the transient shown in Fig. 3 and considering that our previous characterisation points to phenylene oligomers as the most likely guests inside zeolite-Y, we submitted to laser flash photolysis *p*-tetraphenyl in acetonitrile solution whereby a transient peaking at 465 nm similar to that recorded in zeolite was observed. *p*-Tetraphenyl is easily obtained by Suzuki–Miyaura coupling of 4-biphenyl boronic acid and 4-bromobiphenyl. Fig. 4 shows the transient spectrum recorded for *p*-tetraphenyl in acetonitrile at different delays after the laser pulse. In addition to the transient, fluorescence appearing at negative absorption at about 340 nm was also recorded at short times. As expected, the presence of intense emission ($\lambda_{max}$ 380 nm) upon 266 nm excitation was observed independently in a fluorescence measurement in acetonitrile. This emission of *p*-tetraphenylene is compatible with the emission observed for the KY zeolite (shown in Fig. 2). The transient at $\lambda_{max} = 475$ nm observed in the laser flash photolysis decays in the microsecond time scale with a half-life of 24 μs. This transient was safely attributed to the triplet excited state based on the oxygen quenching. In addition, other possible transient species and, in particular, the radical cation, must exhibit a very different optical spectrum according to the literature for related biphenyl.[9]

In the case of the transient recorded for PPP encapsulated in KY zeolite, the presence of oxygen only exerts a minor influence on the kinetics, but this is not without precedent considering the impeded diffusion of oxygen through the micropore of hydrated zeolites.[1,8] Therefore, based on the similarity of the optical spectra in zeolite and acetonitrile solution for *p*-tetraphenyl, the transient observed in the laser flash photolysis of zeolites was attributed to the corresponding triplet excited state of encapsulated phenylene oligomers. The minor differences between the spectrum of *p*-tetraphenyl and that recorded for PP in KY can be due to the presence of a distribution of oligophenylenes and/or the presence of residual Pd atoms on the zeolite.

## Conclusion

By applying the Suzuki–Miyaura conditions using a palladium-containing basic zeolite, it has been possible to produce a zeolite that incorporates phenylene oligomers. The solid exhibits the characteristic photoluminescence spectrum of polyphenylene polymer although somewhat broader. Comparison of the laser flash photolysis spectrum of *p*-phenylene oligomers encapsulated within Y zeolite with the spectrum recorded for *p*-tetraphenyl has allowed assigning the transient to the corresponding triplet excited state.

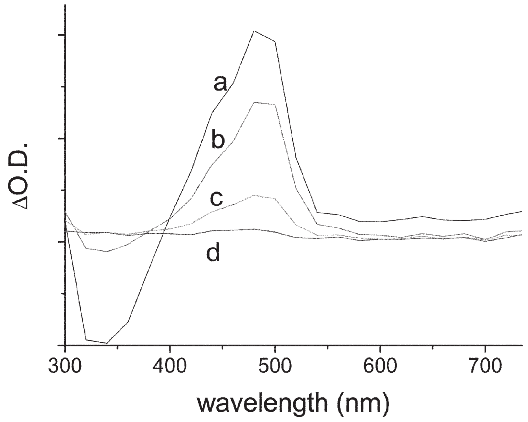

**Fig. 4** Diffuse-reflectance UV-Vis transient spectra recorded for argon purged *p*-tetraphenyl in acetonitrile after 266 nm laser excitation. The spectra have been recorded at 2.4 (a), 6.8 (b), 24 (c) and 64 (d) μs delay.

## Experimental

The reagents and solvents were obtained from commercial sources and used as received. The KY zeolite was prepared through two consecutive ion exchanges starting from a 1 M solution of potassium acetate in bidistilled water and NaY-zeolite (CBV-100, PQ industries). A dispersion of 1 g of zeolite in 5 mL of solution was stirred for 5 h at 80°. Chemical analysis reveals that the level of $Na^+$-to-$K^+$ exchange was 85%. The $PdCl_2$–KY was obtained by the incipient wetness methodology. In this methodology, the required $PdCl_2$ amount to achieve the target loading 1% (16 mg × $g^{-1}$ of zeolite) of palladium in the support was dissolved in the volume corresponding to the pore of the support (1 mL) in order to fill all the voids of the solid without loss of metal.

### Synthesis of PP loaded $PdCl_2$–KY

1,4-Phenylenediboronic acid (146.4 mg, 0.6 mmol) in toluene (20 mL) was magnetically stirred at 110 °C for 48 h in the presence of 2 g of $PdCl_2$–KY. The solution was filtered hot and the solid was submitted to Soxhlet extraction (ethanol and dichloromethane). The solid was dried under reduced pressure ($10^{-1}$ bar) for 6 h.

### Synthesis of non-encapsulated PP

For the sake of comparison a sample of pure non-encapsulated PP was obtained using the same conditions as those for PP loaded PdCl2-KY, using $PdCl_2$ (20 mol%) as palladium reagent and $K_2CO_3$ as base. When polymer precipitation was observed, the solution was filtered hot and the obtained solid was washed in boiling water until no dissolved palladium species were observed in the aqueous phase. The black solid was dried under reduced pressure ($10^{-1}$ bar) for 6 h and the chemical combustion analysis was found $C_6H_4$.

### Synthesis of *p*-tetraphenyl

4-Bromobiphenyl (1 mmol) and 4-biphenyl boronic acid (1.25 mmol) were dissolved in acetonitrile (10 mL). Then, NaAcO (1.5 mmol) and $Pd_2(dba)_3$ (0.05 mmol) were introduced in a vessel and the solution was added. The mixture was placed in a preheated oil bath at 60 °C and stirred magnetically for 24 h. After cooling, the mixture was filtered and the solvent was removed under vacuum. The extract was dissolved in dichloromethane and extracted with water and brine. The organic phase was dried, the solvent evaporated under vacuum and the residue submitted to column chromatography. The product was characterised by GC-MS, $^1$H-NMR and $^{13}$C-NMR.

### Photophysical measurements

Fluorescence spectra were recorded on an Edinburgh Analytical Instruments FL900 spectrophotometer. Laser flash photolysis experiments were carried out using the fourth (266 nm, ≤20 mJ × $pulse^{-1}$) harmonic of a Surelite Nd-YAG laser for excitation (pulse ≤10 ns). The signal from the monochromator/photomultiplier detection system was capture by a Tektronix 2440 digitizer and transferred to a computer that controlled the experiment and provided suitable processing and data storage capabilities.[10]

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