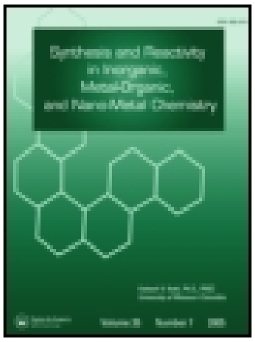

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SORPTION PROPERTIES TOWARDS ENVIRONMENTALLY IMPORTANT VOCs of HALF-SANDWICH Ru(II) COMPLEXES CONTAINING PERYLENE-BIS-IMIDE LIGANDS

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Abstract

Two py-functionalized perylene-bis-imide ligands were synthesized and used to make bimetallic half-sandwich Ru(II) complexes. These were characterized by IR, ^{1}H NMR, ^{13}C CPMAS SSNMR spectroscopy and elemental analysis. The complexes are wheel-and-axle compounds where the axle is the divergent ligand and the wheels are the [(p-cymene)$RuCl_2$] units. The complexes, but not the free ligands, showed absorption of VOCs such as toluene and xylenes through heterogeneous solid-gas uptakes. The reactivity is ascribable to the waa geometry, likely by an upset of the high stacking characterizing the crystalline frameworks of the free ligands. The kinetic profiles of the uptake reactions were determined.

Introduction

Perylene tetracarboxylic acid bisimides, hereafter referred as PBIs, are highly insoluble compounds, characterized by high thermal stability, chemical inertness and light- weather-fastness, characteristics which have made them useful pigments especially for surface-coating in the automotive industry. PBI pigments receive a lot of attention as n-type semiconductor too, due to their high electron-affinity which makes them highly promising materials for organic field effect transistors.[1-3] Functionalization of the imide nitrogens or of the polycyclic scaffold, the so-called perylene-bay, with coordinating functions, allows the preparation of PBI-containing organometallic compounds with different supramolecular architectures, which are of interest in the development of fluorescent based sensors[4-7] or supramolecular aggregates.[8,9] A review concerning the metal-complexes containing rylene (and then also perylene) ligands has recently appeared.[10] N,N'-bis(4-aminopyridine)-3,4,9,10-tetracarboxy-bis-imide and *N*,*N*'-bis(4-aminomethylene)-3,4,9,10-tetracarboxy-bis imide (**L1** and **L2** in Figure 1) are divergent bidentate ligands which can give rise to dinuclear complexes. With **L1** the two metals are separated by a linear and rigid spacer, a good prerequisite in order to build wheel-and-axle (waa) compounds. These are morphologically irregular molecules based on a linear spacer connecting two relatively bulky groups. The irregular shape of waa compounds frustrates the close packing principle and their solid-state chemistry is consequently characterized by the tendency to crystallize as solvates or clathrates.[11] In general, the flexible crystalline framework which characterizes waa compounds allows the introduction of guest species by heterogeneous solid/gas uptake processes into the waa host framework, as demonstrated by us with several organometallic waa complexes containing [(*p*-cymene)$RuCl_2$] wheels.[12-15] These inclusion processes occur with structural rearrangements of the host framework necessary in order to accommodate the incoming guest molecules, which are possible only when the host-guest interactions can compete with the host-host ones. The analysis of the X-ray structures of several PBIs reveals extended stacking between the large π-surface of the perylene cores.[16,17] These strong intermolecular interactions are expected to inhibit the insertion of guest species through heterogeneous gas-uptake processes. However, the large π-surface of the perylene core could be exploited in order to trigger on π-π interactions with aromatic volatile organic compounds (VOCs), such as toluene or the p-xylene isomers, giving rise to host-guest species. This might be facilitated by the introduction of the organometallic wheels, since they are expected to upset the high stacking between the perylene platforms,[18] making the packing more flexible and then more reactive towards VOCs. Monitoring of aromatic VOCs has important environmental concerns, and then molecular solids able to absorb them are highly desirable for their detection and/or capture. The possibility of clathrating aromatic compounds by metal complexes is a well- known phenomenon. Octahedral metal complexes with the general formula ML_4X_2 (M = transition metal, L = py ligand, X = anion), the so-called Werner type complexes, form clathrates with different aromatics from the liquid phase, as reported by different authors in 1957.[19,20] More recently, Werner type complexes were described to be able to form clathrates with xylene isomers also by solid-gas heterogeneous reactions, in some cases with high/moderate selectivity,[21,22] although the initial phases are not porous. This ability was tentatively attributed to conformational flexibility of the host complexes.[23] The development of well-defined molecular solids able to clathrate VOCs has potential applications in several important fields, such as pollution control, separation techniques and heterogeneous catalysis. Thus, the ligands **L1** and **L2** and their ruthenium complexes **1** and **2** were subjected to vapor absorption experiments of toluene and the three xylene isomers, under identical experimental conditions. The use of ligand **L2** and its complex **2** allows testing the effect that the perturbation of the linearity and rigidity of the spacer has onto the uptake properties of the corresponding complex, keeping constant the affinity towards aromatic VOC dictated by the perylenic core. The comparison of the reactivity observed for the free ligands and the corresponding complexes will elucidate the importance of the introduction of the organometallic units [(*p*-cymene)$RuCl_2$] on the sorption properties of these PBI-based solids. An isothermal kinetic analysis of the uptake reactions will also be shown.

Results and Discussion

The synthesis of the ligands **L1** and **L2** was accomplished by following literature reported methods describing the synthesis of PBI ligands (Figure 1).[24] These consider a prolonged reflux of a DMF solution containing perylene-3,4,9,10-tetracarboxydianhydride and an excess of the appropriate amine. The progress of the reactions could be conveniently monitored by FTIR analysis conducted on small samples of the reactant mixtures withdrawn at regular intervals of time, monitoring the disappearance of the anhydride C = O stretching band (1772 cm^{-1}) in favor of the imide C = O stretching bands of the final products (1708 and 1666 cm^{-1} for **L1**, 1691 and 1656 cm^{-1} for **L2**, respectively). The red solids isolated after the workup contained solvent molecules, as established by TGA and elemental analysis, with weight losses percentages of 11.5 and 11.9%, for **L1** and **L2**, respectively, at temperatures higher than 140°C. Desolvation was accomplished by thermal treatment at 140°C (oven, overnight). The purity of the samples was further confirmed by ^{13}C CPMAS SSNMR spectroscopy (the spectra indicated the absence of traces of unreacted dianhydride (Figs S1 and S2 in the Supporting Information). Dissolution of the free ligands in a mixture of CF_3COOD and $CDCl_3$ allowed the recording of their ^1H NMR spectra in solution. In both cases the pyridine protons gave rise to two distinct doublets. All the signals are in the expected chemical shift regions. For the synthesis of the Ru-complexes **1** and **2** two different protocols were followed (Figure 2): a) addition of solid **L1** or **L2** to a dichloromethane solution of $[(p\text{-cymene})RuCl_2]_2$ and subsequent stirring of the mixture for 24 hours at room temperature, or b) heating at 100°C of a cyclohexanone solution of $[(p\text{-cymene})RuCl_2]_2$ containing solid **L1** or **L2** for 24 hours. The workup considers a prolonged washing of the isolated products with dichloromethane where the Ru-dimer precursor is well soluble. This ensure to have the final products free from traces of the unreacted organometallic precursor. The FTIR spectra of the final red solids did not show appreciable changes with respect to the spectra of the starting ligands, as expected for the binding of the Ru-organometallic fragments to the pyridine rings. No differences were observed in the spectra of the complexes prepared in the two different solvents. The same behavior was observed for the decomposition temperatures, which started for all the complexes around 250°C. As seen for the free ligands, also the Ru-complexes are highly insoluble in the common organic solvents. For the recording of the ^1H NMR spectra clear solutions were obtained by dissolving the solids in a few drops of CF_3COOD and diluting with $CDCl_3$. The spectra of **1** and **2** showed the signals of the p-cymene fragment in addition to the signals of the starting ligands, in the expected 2:1 ratio. The elemental analyses of the products were conducted on thermally evacuated samples (oven dried at 140°C for 10 hours) and they were in agreement with the proposed stoichiometries. As regards the reactions conducted in cyclohexanone, complex **1** was initially isolated as cyclohexanone solvate, as indicated by ^1H NMR analysis ($CDCl_3/CF_3COOD$, signals belonging to cyclohexanone at 1.81, 1.97 and 2.48 ppm, see Supporting Information). Cyclohexanone was not detected by FTIR spectroscopy, probably due to overlapping of the C = O stretching band of the ketone with signals belonging to the PBI ligand. Integration of the NMR signals indicated a rough 6 to 1 ratio between cyclohexanone and the complex. However, after storing the solid sample at room temperature the signals belonging to cyclohexanone disappeared giving **1** back. No signals belonging to the solvent were observed in the ^1H NMR spectrum of **2** synthesized in cyclohexanone. ^{13}C CPMAS SSNMR spectra of the complexes were characterized by broad signals, indicative of a rather low crystallinity. However, the absence of signals belonging to unreacted reagents assured high degree of purity for the four isolated complexes (Figs S1 and S2 in the Supporting Information). Unfortunately, owing to the extremely low solubility it was not possible to structurally characterize the Ru-complexes, although many attempts were made in order to isolate X-ray quality single crystals. The wheel-and-axle geometry of the complexes **1** and **2** prompted us to undertake a study on their sorption properties towards environmentally important VOCs, such as toluene, o-, m- and p-xylene, in comparison with the ones shown by the free ligands **L1** and **L2**. Weighed amounts of the solids were thus kept in contact with the vapors of the chosen VOC at room temperature for different time intervals in a closed H-cell reactor (see Fig. S4 in the Supporting Information). Initially, the amount of adsorbed VOC was tentatively determined by weighing the sample before and after the adsorption, but it soon appeared that the host-guest systems formed were highly unstable in the absence of guest-vapors, as evidenced by the continuous and rapid weight loss observed on the balance plate. This high instability prevented TGA analysis. The attempts made to monitor the uptake processes by ^{1}H NMR analysis conducted on freshly prepared samples was again hampered by the fast guest release and led to not fully reproducible data. This can be inferred by Figure 3 which shows the ^{1}H NMR spectra quickly recorded after having exposed complex **1** to p-xylene vapors for one week (spectrum 1), and after having stored the same sample at room temperature in the absence of the aromatic compound for 40 minutes (spectrum 2) and 2 days (spectrum 3), respectively. Nevertheless, the NMR analysis gave evidences of the absorbing capacity of the complexes towards VOCs as well as of the inertness of the free ligands. Due to the high instability of the final materials an exact quantification of the amount of absorbed VOCs was impossible. However, based on the NMR integrals a rough complex/VOC ratio of 1 to 2.5 was estimated for both complexes. During the uptake processes no color changes of the solids were observed. In order to reliably quantify the amount of absorbed VOCs and establish the sorption kinetic profiles of the uptakes, isothermal kinetic studies were undertaken. On the basis of the similar behavior shown by the four complexes during the preliminary uptake experiments we initially restricted the sorption kinetic profile study to complexes **1** (synthesized in dichloromethane) and **2** (synthesized in cyclohexanone), using toluene as VOC, comparing the results with those collected with the free ligands **L1** and **L2**. The uptake reactions were now carried out using a microbalance which monitors the weight change as a function of time under controlled conditions of temperature and pressure. The apparatus employed is reported in Figure 4.[25] Figure 5 shows the absorption profiles observed at 35°C for the toluene sorption. The sorption profiles clearly indicate that the introduction of the organometallic moieties activates the PBI systems towards the uptake of toluene, since the two free ligands are completely inert. With both complexes the uptake occurs speedily and within 50 minutes the sorption curves reach a plateau corresponding to about 25% weight of absorbed toluene. Prolonged exposures did not bring to significative variations. In light of these results, the study was extended to the three xylene isomers. Table 1 collects the amount of VOCs absorbed by the two complexes at 35°C. The results indicate a similar behavior for **1** and **2**, irrespective to the VOC used, with weight percentages of absorbed guest ranging from about 18 to 24.5%, corresponding to 3 molecules of guest for each molecule of dinuclear complex. Noteworthy is the fact that the introduction of the organometallic wheels makes the complexes reactive towards VOCs, whereas the introduction of a methylene spacer between the imide nitrogen and the pyridine ring, as in ligand **L2**, is not sufficient to overcome the high stacking of the perylene platforms.[18] Regrettably, the lack of crystallographic information impedes to highlight the structural differences responsible of the different reactivity found, although it can be concluded that the responsiveness of the complexes to VOCs is dictated by the combination between the waa geometry and the perylene spacer. The sorption curves were finally converted into α-time curves[28] (see Fig. S5 and S6 in the Supporting Information) and fitted into standard kinetic models using the α range of 0.1 to 0.95 to determine the model of sorption. Good fits ($r^2 > 0.993$) of the experimental data were obtained for several models, as indicated in Tables 2 and 3. However, it can be concluded that R3 model showed dominance over the other models with the exception of the system **1**/m-xylene which was better fitted with the R2 model. Hence, it can be concluded that the VOCs uptake by complexes **1** and **2** is governed by a geometrical model.[28] For complex **2** and its free ligand **L2** a BET analysis was carried out in order to measure the surface areas and then the porosity of the samples (see Table S2 and Figure S7 in the Supporting Information). In both cases the values of the experimentally determined surface areas were very low (8.68 ± 0.08 m^2g^{-1} and 4.60 ± 0.07 m^2g^{-1}, respectively) pointing to the absence of intrinsic porosity. Because of the similar uptake behavior, BET analyses were not carried out for the couple **2**/**L2**. The ability shown by the complexes to absorb VOCs must then be imputed to the so called "porosity without pores",[29] to say the ability of the crystalline framework to rearrange once exposed to suitable guests in order to allow its entrance.

In conclusion, two dinuclear half-sandwich Ru(II) complexes containing two different PBI ligands with a wheel-and-axle geometry have been synthesized and characterized. These complexes, differently from their free ligands, are able to absorb aromatic volatile organic compounds, such as toluene and the three xylene isomers, through heterogeneous solid-gas reactions. This ability must be ascribed to the introduction of the half-sandwich organometallic units, which possibly work by reducing the stacking of the perylene moieties thus making the corresponding solids more responsive. The isothermal kinetic profiles of the uptakes indicate a geometrical model but, currently, the lack of structural information hampers the definition of a plausible sorption mechanism. These results are nonetheless stimulating for the development of other PBI based organometallic systems with responsive character towards VOCs which could find application in all the fields where the VOC monitoring is essential.

Experimental

All the manipulations have been carried out under an atmosphere of dry nitrogen, using oven dried Schlenk vessels and freshly distilled solvents. Perylene-3,4,9,10-tetracarboxylic dianhydride, 4-aminopyridine and 4-aminomethylpyridine were purchased from Aldrich and used as received. [(p-cymene)RuCl$_2$]$_2$ was synthesized as reported in literature.[30] ^{1}H NMR spectra were recorded on an Avance-300 or Avance-400 Bruker spectrophotometers at 25°C and the chemical shift values are referred to TMS (for SSNMR measurements see Supporting Information). IR (ATR) spectra were collected by means of a Nicolet-Nexus spectrophotometer in the range 4000-600 cm^{-1} by using a diamond crystal plate, or by KBr plates on a Thermo Avatar spectrophotometer, in the 4000-400 cm^{-1} range. Elemental analyses were performed by using a FlashEA 1112 Series CHNS-O analyzer (ThermoFisher) with gas-chromatographic separation. TGA analyses were conducted by means of a Perkin Elmer TGA7 apparatus, with a heating rate of 5°C min^{-1} from 25°C to 250°C, under an atmosphere of dry nitrogen.

Synthesis of ligands L1 and L2

Perylene tetracarboxydianhydride (0.5 g, 1.27 mmol) and the appropriate amine were placed in a Schlenk vessel under a flow of dry nitrogen, together with a magnetic bar. 15 mL of anhydrous DMF saturated with nitrogen were introduced by syringe and the reactor was sealed with a teflon stopcock. The mixture was heated at 130°C monitoring the progress of the reaction by FTIR spectroscopy (disappearance of the C = O stretching bands of the starting anhydride in favor of the C = O stretching bands of the imide groups). The FTIR monitoring was performed as follows: about 0.5 ml of the reaction mixture was withdrawn at regular time intervals by a pipette, the sample was diluted with dichloromethane and the solid collected by centrifugation. After washing with diethyl ether and vacuum drying the solid was analyzed by FTIR (ATR). Typically, the synthesis of **L1** reached completion after 48-72 hours, while the synthesis of **L2** reached completion within 24 hours. The final purple solids undergone the same workup described for the FTIR samples. In order to completely remove DMF **L1** and **L2** were oven dried at 140°C overnight.

N,N′-bis(4-pyridine)perylene-3,4,9,10-bis-dicarboxydiimide (**L1**) Yield: 86%. M.p.: > 350°C. Anal. Calcd. for $C_{34}H_{16}N_4O_4{\cdot}\frac{1}{2}DMF$ (581.07): C, 73.38; H, 2.59; N, 7.40. Found: C, 73.20; H, 3.00; N, 7.84. ^{1}H NMR ($CF_3COOD/CDCl_3$): δ9.18 (d, 4H, py, $^3J_{HH}$ = 6Hz), 8.95 (s, 8H, perylene), 8.27 (d, 4H, py, $^3J_{HH}$ = 6Hz). FTIR (KBr, cm^{-1}): 1708 (C = O), 1666 (C = O), 1590, 1576, 1361, 1346, 709, 734, 639. TGA (from 25°C to 250°C, 10°C/min, under nitrogen atmosphere): loss of 11.5% in the T-interval 140-190°C.

2.1.2. N-N′-bis(4aminomethylpyridine)perylene-3,4,9,10-bis-dicarboxydiimide (**L2**) As for **L1** but using 4-aminomethyl pyridine instead of 4-aminopyridine. Yield (95%). M.p.: >350°C. Elemental analysis calcd. for $C_{36}H_{20}N_4O_4 \cdot 1/2DMF \cdot 1/2H_2O$ (618.135): C, 72.86; H, 3.99; N, 10.19. Found: C, 72.73; H, 3.38; N, 10.09. ^{1}H NMR ($CF_3COOD/CDCl_3$): δ8.85 (m, 12H, py+perylene), 8.17 (d, 4H, py, $^3J_{HH}$ = 6.6Hz), 5.75 (s, 4H, CH_2). FTIR(KBr, cm^{-1}): 1691 (C = O), 1656 (C = O), 1594, 1578, 1341, 811, 749, 644. TGA (from 25°C to 250°C, 10°C/min, under nitrogen atmosphere): loss of 11.9% in the T-interval 140-190°C.

Synthesis of the Ru-complexes 1 and 2

Synthesis in dichloromethane

[(*p*-cymene)$RuCl_2$]$_2$ (0.1 g, 0.163 mmol) was placed in a Schlenk tube equipped with a stirring bar and dissolved in 30 ml of anhydrous dichloromethane under a dry nitrogen atmosphere. The appropriate ligand was introduced as solid and the deep red mixture was stirred at room temperature for 24 hours. Then, the deep red solid was collected by centrifugation, plenty washed with dichloromethane in order to remove possible traces of unreacted Ru-dimer and then washed with diethyl ether and finally vacuum dried at 100°C.

*{[(p-cymene)RuCl$_2$]$_2$(**L1**)}* (**1**) Yield (90%). M.p.: 251.6°C. Anal. Calcd. for $C_{54}H_{44}Cl_4N_4O_4Ru_2$ (1156.9): C, 56.06; H, 3.83; N, 4.84. Found: C, 56.21; H, 3.70; N, 5.01. .^{1}H NMR ($CF_3COOD/CDCl_3$): δ9.13 (d, 4H, py, $^3J_{HH}$ = 6.6Hz), 8.89 (s, 8H, perylene), 8.22 (d, 4H, py, $^3J_{HH}$ = 5.1Hz), 5.61 (d, 4H, cymene, $^3J_{HH}$ = 6Hz), 5.42 (d, 4H, cymene, $^3J_{HH}$ = 6Hz), 2.78 (m, 2H,

C*H*(CH$_3$)$_2$), 2.22 (s, 6H, CH$_3$), 1.30 (d, 12H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9Hz). FTIR (KBr, cm^{-1}): 3055, 2962, 1701 (C = O), 1668 (C = O), 1592, 1576, 1357, 809, 746, 654.

*{[(p-cymene)RuCl$_2$]$_2$(**L2**)}* (**2**) Yield (94%). M.p.: 247.4°C. Anal. Calcd. for $C_{56}H_{48}Cl_4N_4O_4Ru_2$ (1184.95): C, 56.76; H, 4.08; N, 4.73. Found: C, 56.39; H, 4.06; N, 4.74. ^{1}H NMR (CF$_3$COOD/CDCl$_3$): δ8.82 (m, 12H, perylene+py), 8.12 (d, 4H, py, $^3J_{HH}$ = 5.4Hz), 5.71 (s, 4H, CH$_2$), 5.61 (d, 4H, cymene, $^3J_{HH}$ = 6Hz), 5.42 (d, 4H, cymene, $^3J_{HH}$ = 6Hz), 2.77 (m, 2H, C*H*(CH$_3$)$_2$), 2.22 (s, 6H, CH$_3$), 1.29 (d, 12H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9Hz). FTIR (ATR, cm^{-1}): 1694 (C = O), 1657 (C = O), 1593, 1343, 810, 748.

Synthesis in cyclohexanone

The reactions were carried out at 100°C in a teflon stopcock sealed rotaflow reactor, using cyclohexanone as solvent. The amount of reagents and the concentrations of the reactant solutions were as for the reactions conducted in dichloromethane. Complex **1** was initially isolated as **1**·6C$_6$H$_{10}$O, as indicated by the ^{1}H-NMR analysis (CDCl$_3$/CF$_3$COOD, signals belonging to cyclohexanone at 1.81, 1.97 and 2.48 ppm). However, at room temperature **1**·6C$_6$H$_{10}$O desolvates giving **1** back within 24-36 hours, as established by ^{1}H-NMR. A complete desolvation could be accomplished by heating the solvate complex at 140°C under vacuum for 10 hours. Complex **2** was isolated as an unsolvated species, whose characterization (IR, ^{1}H-NMR and elemental analysis) was equivalent to that of complex **2**.

Sorption kinetics of volatile organic compounds by ruthenium complexes

Both **1** and **2** were dried under a vacuum for 5hrs at 95°C before being exposed to solvent vapors of o-xylene, p-xylene, m-xylene and toluene. Kinetic studies were carried out to analyze the uptake of volatile organic compounds by the activated samples of **1** and **2** at 35°C. Samples weighing between 80 and 95 mg with particle size in the range of 38-45 µm were used. A balance, placed in a thermostatically controlled oven (precision ca. 0.5°C), is connected to a computer which tracks the experiment. A sample holder is contained within a brass cylinder which has six solvent chambers evenly distributed around the central sample container. The brass container fits over the sample on the balance and can be sealed. The solvent was placed in the six solvent chambers, the container sealed and the vapor pressure allowed to equilibrate for 30 minutes. The scale was zeroed, the seal between sample and solvent vapor removed and the monitoring computer program (PB303S31) started. The increase in mass with time was recorded and then fitted to analyze the extent of reaction with time.

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Table 1 Amounts of absorbed VOCs by complexes **1** and **2** during the uptake experiments conducted at 35°C.

Sample ID	VOC	Amount used/ mg	Amount absorbed/mg	%weight absorbed[b]	G/H
1	m-x	80	21.6	21.26	2.9
1	o-x	80	24.2	23.22	3.3
1	p-x	95	27.5	22.45	3.2
1	tol	95	25	20.83	3.3
2	m-x	95	30.9	24.54	3.6
2	o-x	80	21.8	21.41	3.0
2	p-x	80	17.6	18.03	2.5
2	tol	95	25	20.83	3.4

[b] Calculated as {[mass VOC]/[mass of (H+VOC)]}x100, where VOC = adsorbed VOC, H = host (*i.e.* complex **1** or **2**)

Table 2 Analysis of the uptake of VOCs by **1** at 35°C.

Solvent	Kinetic model	R^2	Rate constant, k (min^{-1})
ortho-xylene	(R3) $1 - (1 - \alpha)^{1/3}$	0.997	5.36E-2
	(D2) $(1 - \alpha) \ln (1 - \alpha) + \alpha$	0.994	6.25E-2
meta-xylene	(R2) $1- (1- \alpha)^{1/2}$	0.996	2.51E-2
	(R3) $1 - (1 - \alpha)^{1/3}$	0.997	2.10E-2
para-xylene	(R2) $1- (1- \alpha)^{1/2}$	0.999	1.05E-2
	(R3) $1 - (1 - \alpha)^{1/3}$	0.996	8.55E-3
Toluene	(R3) $1 - (1 - \alpha)^{1/3}$	0.995	1.95E-2
	(D2) $(1 - \alpha) \ln (1 - \alpha) + \alpha$	0.996	2.67E-2
	(D4) $[1 - 2\alpha/3] - (1 - \alpha)^{2/3}$	0.999	1.75E-2

Table 3 Analysis of the uptake of VOCs by **2** at 35°C.

Solvent	Kinetic model	R^2	Rate constant, k (min^{-1})
ortho-xylene	(R3) $1 - (1 - \alpha)^{1/3}$	0.999	2.55E-02
	(R2) $1- (1- \alpha)^{1/2}$	0.996	2.18E-02
meta-xylene	(R2) $1- (1- \alpha)^{1/2}$	0.995	3.63E-02
	(R3) $1 - (1 - \alpha)^{1/3}$	0.983	3.01E-02
para-xylene	(R2) $1- (1- \alpha)^{1/2}$	0.993	1.79E-02
	(R3) $1 - (1 - \alpha)^{1/3}$	0.996	1.59E-02
	(D2)$(1 - \alpha) \ln (1 - \alpha) + \alpha$	0.998	2.24E-02
	(D4) $[1 - 2\alpha/3] - (1 - \alpha)^{2/3}$	0.996	6.86E-03
Toluene	(R2) $1- (1- \alpha)^{1/2}$	0.999	3.04E-02
	(R3) $1 - (1 - \alpha)^{1/3}$	0.999	2.31E-02

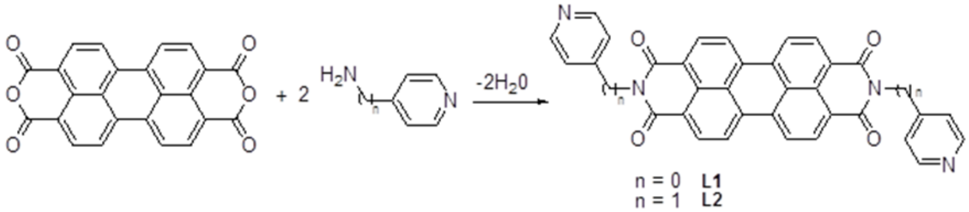

Figure 1 Synthesis of the PBI ligands L1 and L2

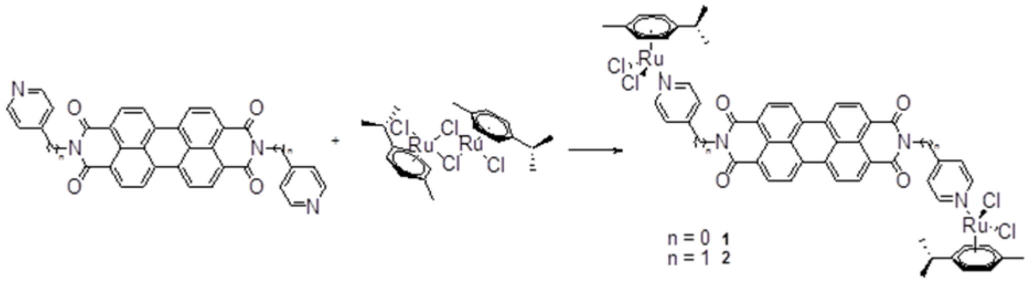

Figure 2 Synthesis of the Ru-complexes 1 and 2

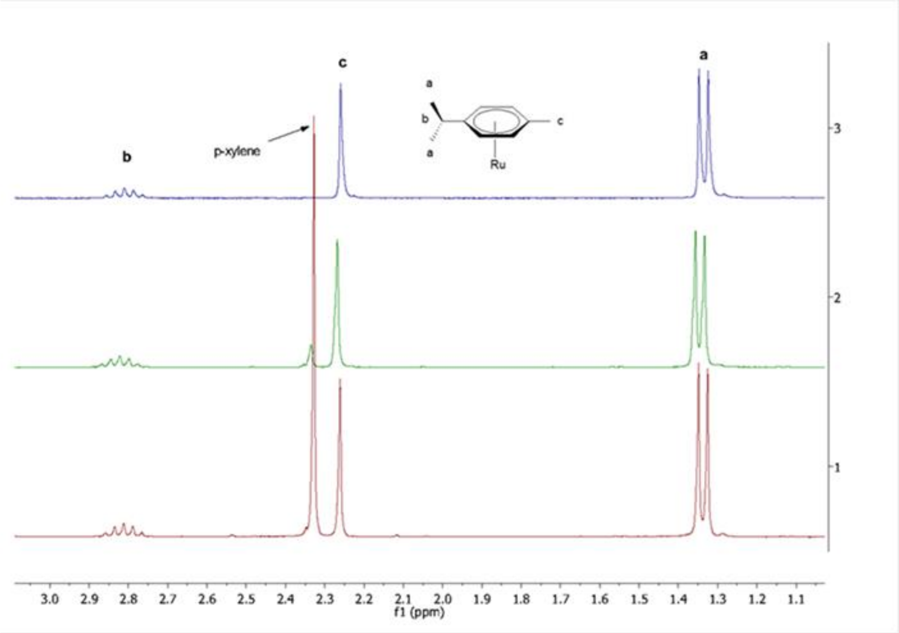

Figure 3 1H-NMR spectrum (aliphatic region) of 1/p-xylene (px) at different time intervals: immediately after the uptake reaction (spectrum 1), after 40 minutes at rt in the absence of px vapors (spectrum 2), after 2 days at rt in the absence of px vapors (spectrum 3).

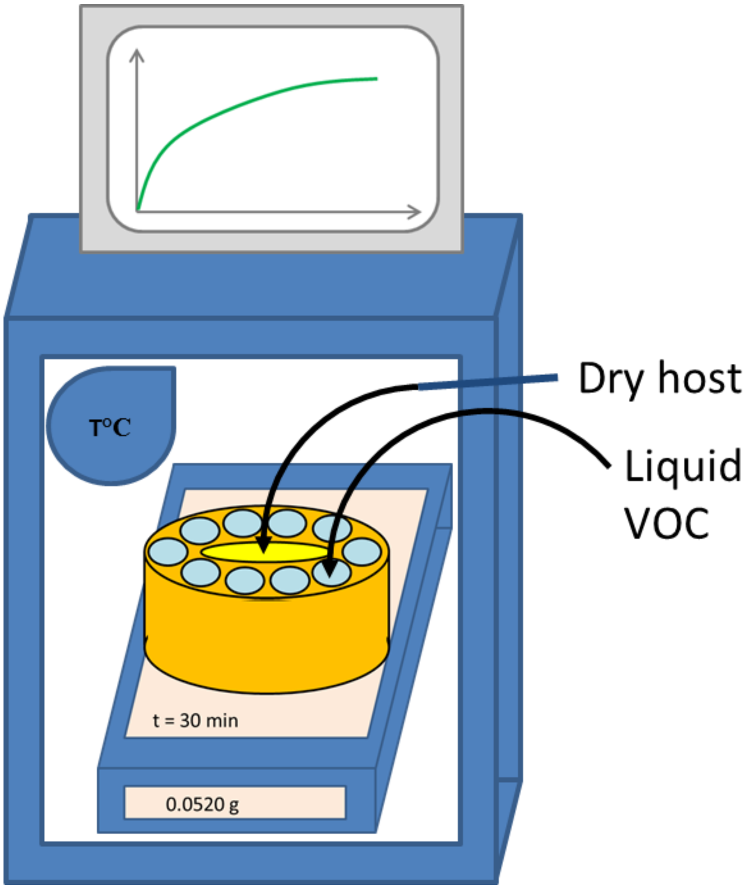

Figure 4 Apparatus used for the sorption kinetics of VOCs. After charging with the solid host sample and liquid VOC the brass cylinder is sealed (cover not shown in the figure) and the vapor pressure allowed to equilibrate for 30 minutes at the desired temperature.

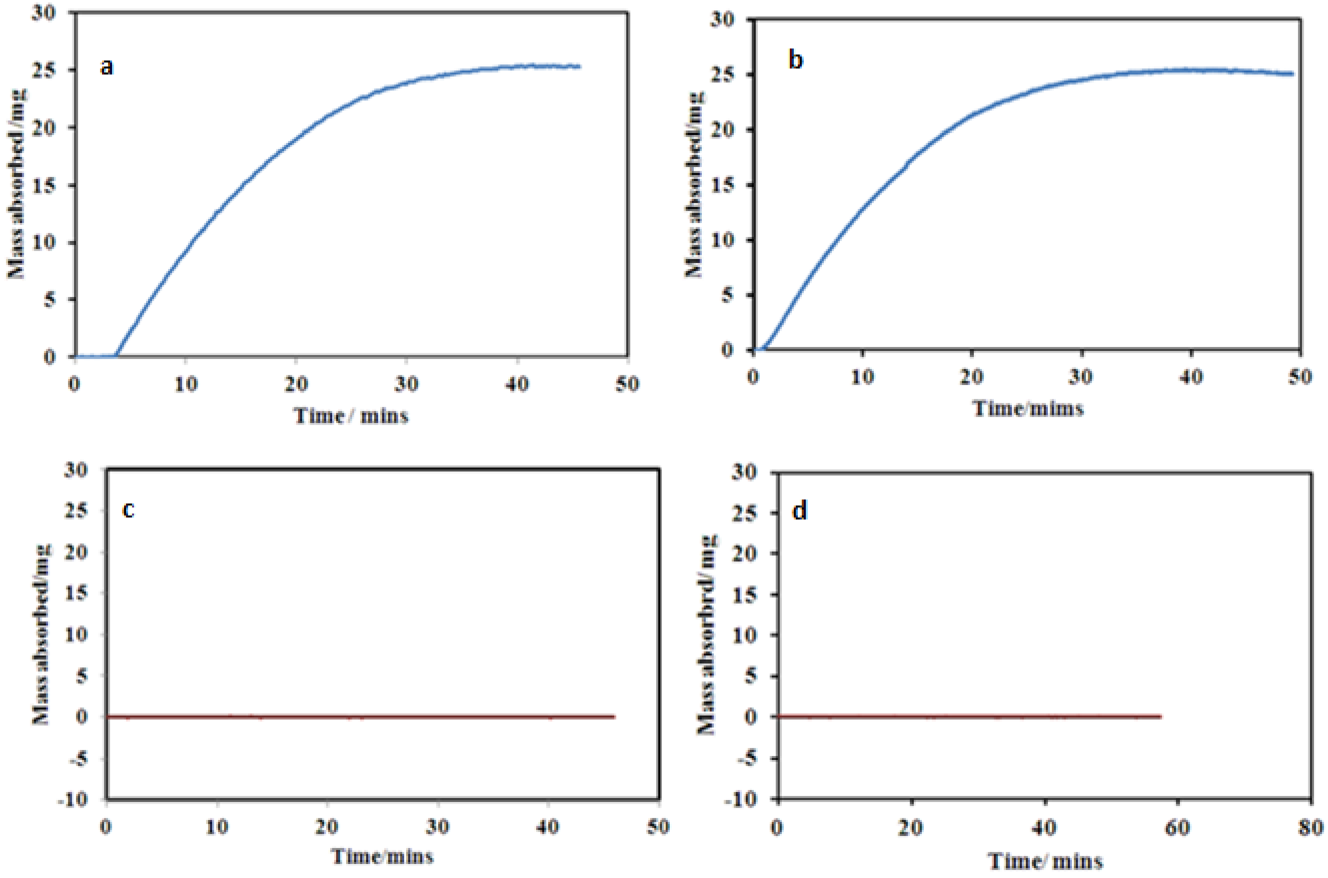

Figure 5 Profiles of the uptakes of toluene at 35 °C for 1 (a), 2 (b), L1 (c) and L2 (d).