SUPPLEMENTARY INFORMATION

for the article:

Fast transport of HCl across a hydrophobic layer over macroscopic distances by using a Pt(II) compound as the transporter

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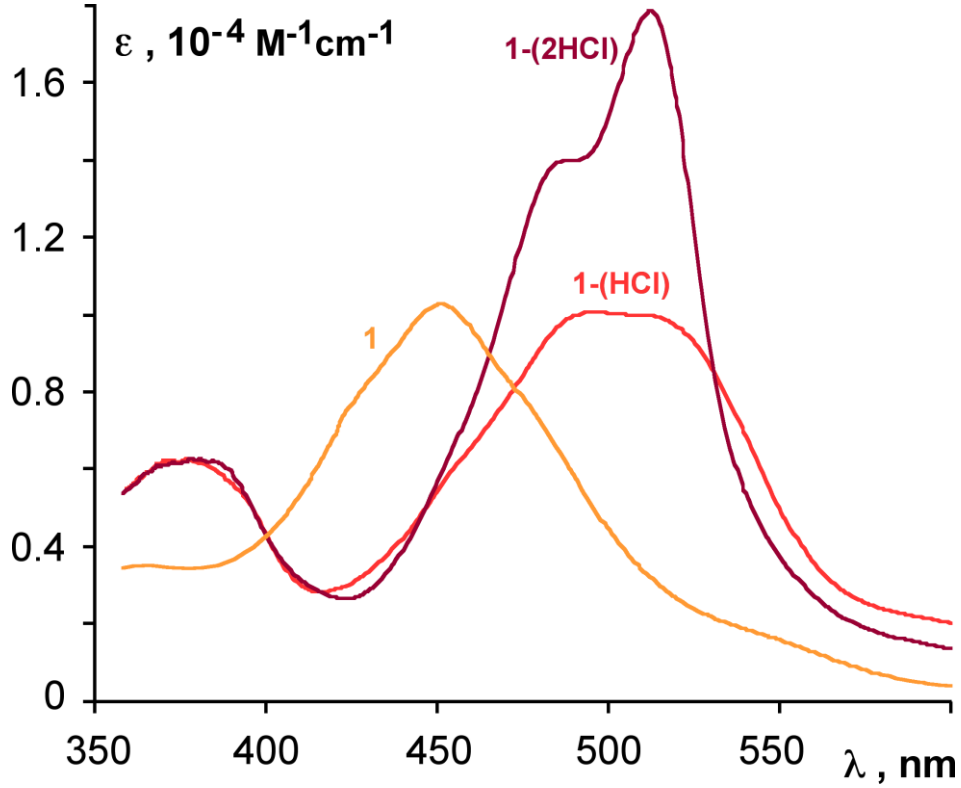

Figure S1. Absorption spectra of the independently prepared species **1**, **1-HCl** and **1-(2-HCl)** in chloroform solution (see also ref. S1).

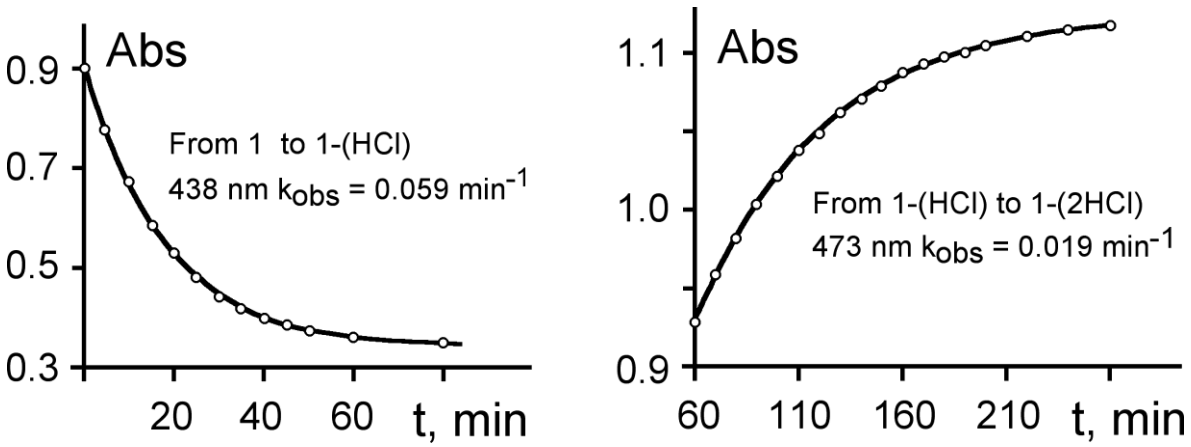

Figure S2. Kinetics of the sequential steps of HCl uptake, leading from **1** to **1-(HCl)** and finally to **1-(2HCl)**, using 2 cm^2 -wide cuvettes. The measured rate constants (inset) are roughly twice than those obtained by using 1 cm^2-wide cuvettes (0.032 min^{-1} and 0.010 min^{-1} for the first and second process, respectively), shown in the Figure 3 of the main text. Temperature, here as well as for all the other HCl uptake and release processes described in the work and for the U-tube experiments, was 298 K.

*Fast mobility of HCl in the tight ion pairs **1-HCl** and **1-(2HCl)***

The key for understanding the fast mobility of HCl in chloroform solution of **1**, **1-HCl**, and **1-(2HCl)** is offered by the fast exchange of coordinated HCl, as demonstrated by NMR studies.[S1] Actually, NMR experiments indicate that in **1-HCl** the coordinated HCl is mobile: the NMR of **1-HCl** exhibits only a broad singlet for the N-H-Cl proton and single signals for both the methyl and methylene groups, until temperature as low as 210 K.[S1] This indicates that both coordination sites of the compound experience the same environment, that means that the coordinated HCl is "shared" by both the dithioxamide/dithiooxamidate moieties, therefore involving fast HCl exchange between **1-HCl** molecules. On the contrary, ^{1}H NMR and ^{13}C NMR low temperature spectra of the species {[(R-dithiooxamidate)Pt(H-R-dithiooxamide)]$^{+}$, Cl^{-}}, **3-HCl**, in which R stands for a {S}-1-phenylethyl substituent, show three signals for both methine and methyl hydrogens, corresponding to the species which does not contain HCl and to the species containing one and two coordinated HCl fragments (see Figs. S3 and S4; a further description of the results showed in Figure S3 is discussed later, in *Comments to Fig. 3*). This indicates that the exchange process of HCl between the two N-H…N sites becomes slow on the NMR timescale when the coordination site for HCl is encumbered. Unfortunately, it has not been possible to obtain accurate values of the activation parameters for the above-mentioned dynamic process, because signals of both methine and methyl protons are partially superimposed. However, the coalescence temperature of methine signals allow to get an approximate value (66 s^{-1}) for the rate of HCl exchange at 290 K. Since HCl exchange is clearly much faster in **1** than in **3-HCl**, the above given value for HCl exchange is only a lower limit for **1**. So, for **1** the HCl exchange is expected to occur in the microsecond timescale or faster. A similar dependence of the exchange rate from the steric congestion of the (R)N-H…N(R) site has also been observed in a Rh(III) dithiooxamide complex.[S2]

It should also be noted that the fast HCl exchange between metal complexes cannot be justified only by diffusion. Possibly, HCl exchange takes place via hopping, mediated by the solvent molecules.

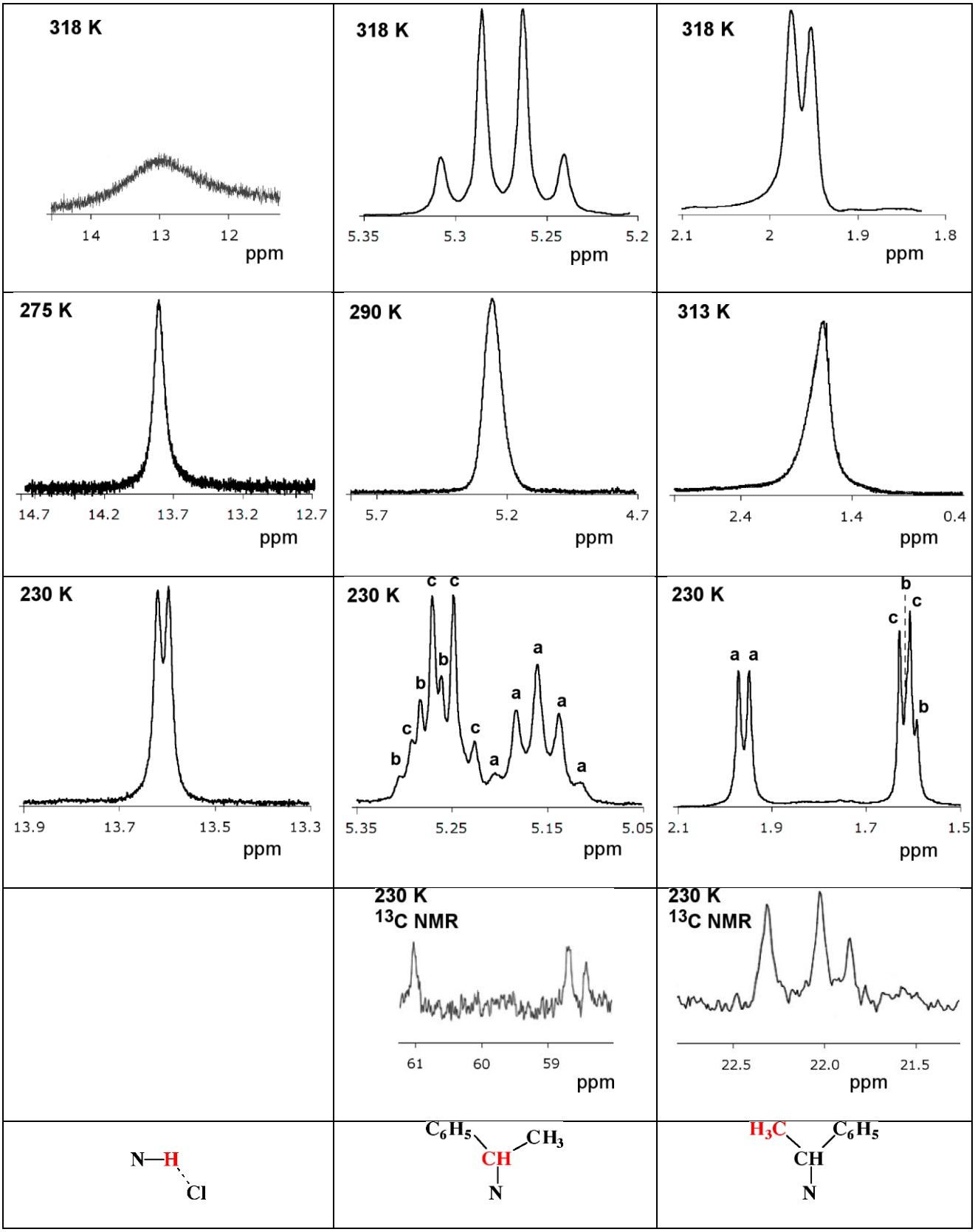

Figure S3. Spectral signals of NHCl group (left column), methine (central column) and methyl protons (right column) of the {S}-1-phenylethyl group of the monohydrohalogenated species **A** (for structural formula, see Figure S4) in chloroform at 318 K (first row), at coalescence temperatures

(second row) and at 230 K (third row). ^{13}C NMR signals of both methine and methyl groups are reported in the fourth row. The CH and CH_3 signals at 230 K are labelled by the letters **a**, **b** and **c**. Peaks labelled as **a** (five lines corresponding to two quartets plus a doublet at higher fields) refer to the fully hydrohalogenated species **C** (see Figure S4). Peaks labelled as **b** (five lines, of whom two are obscured by a superimposed quartet) refer to the hydrohalogenated half moiety of **A**. Finally, peaks indicated as **c** refer to two coincident quartets featuring CH of **A** and **B** (see Figure S4), and to two coincident doublets featuring CH_3 of the dehydrohalogenated half moiety of the species **A** as well as to both halves of the totally dehydrohalogenated species **B**. NHCl signal at 230 K features the amide protons of both **A** and **C**. For further discussion, see *Comments on Fig. 3*.

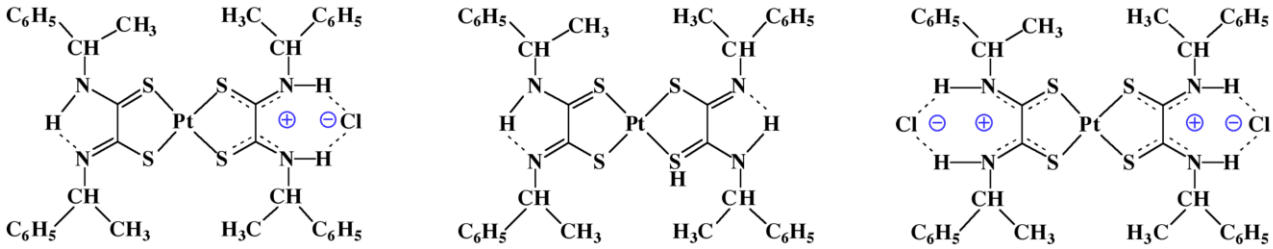

Figure S4. Structural formulae of the species **A**, **B** and **C** mentioned in Figure S3. The compounds are the various hydrohalogenated forms of compound {[(R-dithiooxamidate)Pt(H-R-dithiooxamide)]$^+$, Cl^-} (formally, compound **A** in figure), in which R stands for the {S}-1-phenylethyl group.

Comments to Figure S3

The data in Figure S3 demonstrate that in chloroform solution compound **A**, formally made of a hydrohalogenated dithiooxamide moiety and a dithiooxamidate moiety, undergoes a rapid equilibrium with **B** and **C** species, as a consequence of fast HCl transfer.

Actually, the reported spectra indicate that at high temperature the HCl very rapidly jumps among the two nitrogen N-H…N sites of the molecule. In fact, the two halves of the species **A** yield only one group of signals in the NMR spectra (see first row). In particular, because of the rapid motion of HCl, NH…Cl proton appears in the spectrum as a very broad singlet, while CH methine protons of the dithiooxamide groups are featured by a quartet, since such protons cannot couple with the mobile NH protons. On cooling, after coalescence (second row) the methyl doublet tends to split into two groups of signals, until three doublets appear in the proton spectrum at 230 K (third row). The spectrum does not change anymore on further cooling. The corresponding ^{13}C NMR spectra in the methyl region show the same behaviour: the single methyl signal at 318 K (not shown) splits into three signals at 230 K (fourth row, third column).

As for the dithiooxamide CH protons, the sharp quartet at 318 K (first row, second column) coalesces at 290 K (second row, second column); then, it splits into two groups of signals which at 230 K appear as two groups of five lines and a quartet which is superimposed to one of them (third row, second column). The five line patterns feature CH groups near to the coordinated HCl in **A** and **C** species. In fact, the CH quartet is split by the near amide proton, which is fixed on the amide nitrogen at low temperature, at least on the NMR time scale. Three signals feature the CH system also in the ^{13}C NMR spectrum (fourth row, second column). Finally, the very broad singlet, featuring NHCl at high temperatures, becomes a sharp doublet at 230 K, since the fixed NH proton is split by the near methine hydrogen.

It should be stressed that the above data also indicate that species **A**, as well as species **1-HCl** discussed in the article, is not a single compound in chloroform at room temperature, but is a mixture including also the parent **B** and **C** species (and **1** and **1-2HCl**, in the case of **1-HCl)**.

Comment to Figure 2 of the main text.

In the release process shown in Figure 2 of the main text, a low amount of NaCl or NaOH (to reach a concentration of 10^{-4} M) has to be added in the aqueous phase to perfectly keep the isosbestic points. However, the presence of NaCl or NaOH does not affect the rate constants of the release process.

*Comparison between HCl transport ability of compounds **1** and **2**: further data and discussion*

A series of U-tube experiments in the identical experimental conditions (concentration, temperature, etc.) was made to better compares the HCl transport efficiency of **1**, the Pt(II) symporter here studied, and **2**, a well-known and fast HCl transporter.[S3] In the experimental set-up described in Figure 4 of the main text (absence of solution stirring), the lag time for the appearing of HCl in the receiving phase (measured in close-contact with the chloroform/water interface) is 2.5 min for **1** and 60 min for **2 (**Fig. S5, inset). The efficiency of HCl transport can also be related to the slope of the conductivity vs time curve (flow rate), at the initial times of the transfer process: such a slope is 14 μS/h for **1** and 5.3 μS/h for **2** (Figure S5). Note that, when the appearance of HCl in the receiving face is measured 3 mm above the interface, lag time for **1** is 60 min and for **2** is hours.

The lag time is probably the more interesting parameter: it is mainly related to the rate of HCl transport in *the chloroform phase* and appears that **1** is about 25 times faster than **2** as HCl

transporter. The difference between **1** and **2** is smaller as far as the flow rate is concerned: in fact, the HCl flow rate mainly depends on the interface transfer rates, so leveling off the differences between **1** and **2**. It can also be noted that **2**, although slower than **1** as HCl transporter, is still a quite good HCl transporter, even in the absence of stirring.

Finally, we also performed similar U-tube experiments with stirring the chloroform phase: in these conditions, lag time was 1 min for both **1** and **2**, as expected since diffusion of HCl receptors within the organic phase is extremely increased by stirring; HCl transport flow rate also increases for both **1** and **2** (32 μS/h and 17 μS/h, respectively), also in agreement with the expectations. It is interesting to note that the flow rate of **1** in the absence of stirring is practically equivalent to the flow rate of **2** with stirring.

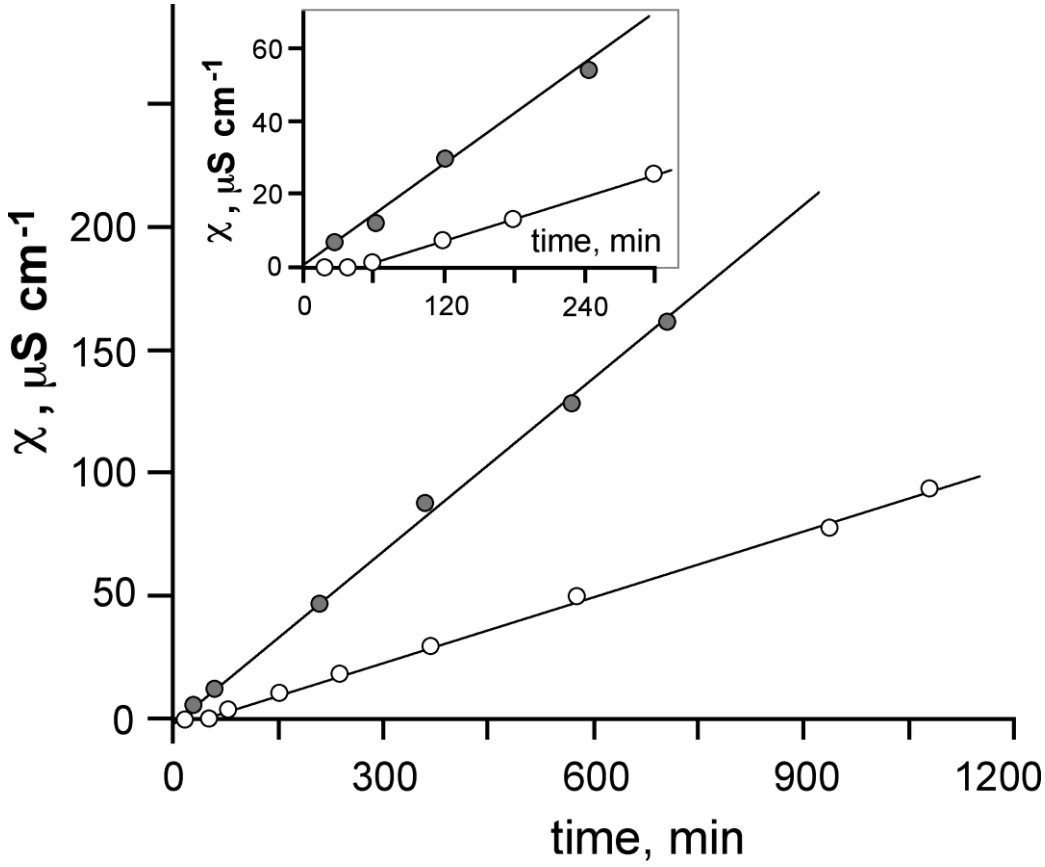

Figure S5. Comparison between the HCl transport properties of the Pt(II) compound **1** and of the model species **2**. HCl transport is measured in U-tube experiments, without stirring. The experiments shown are made in the same conditions described in Figure 4 of the main text. Open circle values are obtained by using **2** as HCl transporter. Solid circle values refer to **1** as HCl transporter. Slopes of the conductivity/time relationship (related to flow rate of HCl transport) are 17 μS cm^{-1} h^{-1} and 5.3 μS cm^{-1} h^{-1} for **1** and **2**, respectively. In the inset, difference in lag time is also evidenced, giving information on the speed of HCl transport phenomena using **1** or **2**. Values for stirred systems are given in the former Section of ESI, "*Comparison between HCl transport ability...*" .

References to the supplementary information

S1 A. Giannetto, F. Puntoriero, A. Barattucci, S. Lanza and S. Campagna, *Inorg. Chem.* 2009, **48**, 10397.

S2 S. Lanza, A. Giannetto, G. Bruno, F. Nicolò and G. Tresoldi, *Eur. J. Inorg. Chem.*, 2009, 2647.

S3 K. J. Winstanley, S. J. Allen and D. K. Smith, *Chem. Commun.*, 2009, 4299.