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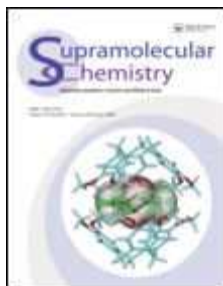
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Cyclophanes Or Cyclodextrins: What Is The Best Host For Aromatic Volatile Organic Compounds ?

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3 Cyclophanes Or Cyclodextrins: What Is The Best Host For Aromatic Volatile Organic
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6 Compounds ?
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10 Paul Ionut Dron, Sophie Fourmentin¹, Francine Cazier, David Landy and Gheorghe
11 Surpateanu
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17 Laboratoire de Synthèse Organique et Environnement (EA2599), Université du Littoral
18 Côte d'Opale, 145 Avenue Maurice Schumann, 59140 Dunkerque, France.
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23
24 **Abstract**
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29 The first results of the complexing ability of cyclobis(paraquat-*p*-phenylene) as
30 supramolecular host with different aromatic volatile organic compounds are presented.
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32 The formation constants of cyclobis(paraquat-*p*-phenylene) with toluene and
33 halogenobenzenes were determined in aqueous solution by static headspace associated
34 with gas chromatography and compared with the ones obtained by cyclodextrins. The
35 data indicated the formation of 1:1 inclusion compounds in both cases. The results
36 underlined a greater complexation ability for cyclobis(paraquat-*p*-phenylene) which was
37 confirmed by a theoretical study.
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51 Keywords: Cyclophanes, Cyclodextrins, Inclusion compounds, Static headspace,
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58 **Introduction**
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Cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) (Figure 1) and its inclusion complexes have drawn much attention because of their many interesting properties and applications especially in the design of nanoscale molecular devices [1,2]. This cyclophane can be employed as a binding probe for studies in molecular recognition. Our interest lies in volatile organic compounds (VOCs) recognition by supramolecular hosts like modified cyclodextrins (CDs) (Figure 1) or cyclophanes [3,4]. Indeed, the internal cavity of CBPQT⁴⁺ has a shape and hydrophobicity that make it a selective inclusion host for aromatic residues [5,6].

Insert Figure 1

Association of CBPQT⁴⁺ with an electron rich aromatic guest produces a colored, charge-transfer complex. Binding constants are then usually determined by monitoring the appearance of this complex using standard spectrometric methods. These methods are not appropriate in the case of VOCs as guest because of the low solubility and the high volatility of these compounds. We have recently developed a method based on static headspace gas chromatography (HSGC) to study the inclusion complex formed between CDs and VOCs [7]. This method has been applied to the determination of the formation constant of the inclusion complexes formed between CBPQT⁴⁺ tetrachloride salt, α -cyclodextrin (α -CD), β -cyclodextrin (β -CD) and randomly-methylated- β -cyclodextrin (RAMEB) with toluene and halogenobenzenes in water.

Results and discussions

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3 In order to evaluate the inclusion ability of the supramolecular hosts, we used a static
4 headspace method. Such a method is based on the variation of the peak area of the VOC
5 observed upon addition of each host in a solution containing the VOC.
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10 The stability constants for the inclusion of VOCs with CBPQT⁴⁺, α -CD, β -CD and
11 RAMEB in aqueous solution were determined at 30°C with four host concentrations
12 (35mM, 20mM, 10mM and 5mM for RAMEB; 7mM, 4mM, 2mM and 1mM for α -CD
13 and β -CD; 0.3mM, 0.2mM, 0.1mM and 0.03mM for CBPQT⁴⁺). The effect of an
14 increased concentration of CBPQT⁴⁺ on the chromatographic peak of toluene is shown
15 in Figure 2.
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28 **Insert Figure 2**
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32 The obtained variations are in good agreement with the 1:1 host/guest ratio, as could be
33 expected from analogous results for other substituted benzene derivatives for
34 cyclophanes [8,9] or cyclodextrins [10-13]. The experimental data obtained for
35 iodobenzene and CBPQT⁴⁺ are given in Figure 3 with the theoretical curve for a 1:1
36 complex with a formation constant of 9459 M⁻¹. As one can see, the experimental points
37 fit well with the theoretical curve.
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53 The formation constants are calculated by an algorithmic procedure [14] and are
54 reported in Table 1 in comparison with literature data (in bracket) [11-13].
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Insert Table 1

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6 There are few references in literature in which HSGC is used for determining stability
7 constants of different compounds with CDs [15-20] and especially for VOCs
8 [13,21,22].
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12 The obtained formation constants are in good agreement with the corresponding ones
13 found in literature for CDs [11-13], while, in the case of CBPQT⁴⁺, the values are in the
14 same order of magnitude than for other aromatic guests in aqueous media [8,9]. The
15 formation constants obtained with CBPQT⁴⁺ are 10 to 100-fold stronger than for CDs,
16 which demonstrates a greater complexation ability of the cyclophane.
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27 In addition, if one plots the logarithm of the formation constant ($\log K_f$) as a function of
28 the molar refractivity (MR) of the substituent (Figure 4), a good linear relationship is
29 obtained for both CBPQT⁴⁺ and β -CD. This linear variation with the size of the
30 substituent shows that Van der Waals interactions are important for the two
31 supramolecular hosts. In addition, it has to be underlined that nearly identical slopes are
32 obtained for the two hosts, whereas a greater intercept is observed for CBPQT⁴⁺. This
33 leads to think that the greater complexation ability of the cyclophane is a consequence
34 of a better encapsulation of the phenyl ring.
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53 In order to get better insights into the mechanisms of complexation, we have also
54 realised a comparative docking study of iodobenzene into CBPQT⁴⁺ and β -CD. The
55 initial CBPQT⁴⁺ structure was in agreement with literature data (geometrical parameters
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3 strictly equal to already published PM3 results) [23-24]. The optimal docked structures
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5 are illustrated in Figure 5.
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15 It can be seen that a very close proximity exists between iodobenzene and CBPQT⁴⁺,
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17 leading to a greater stabilisation by Van der Waals forces than for β -CD inclusion
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19 compound. Indeed, a value of -15.7 kcal/mol is obtained in the case of CBPQT⁴⁺,
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21 against -10.6 kcal/mol for β -CD. Moreover, the existence of charges on the cyclophane
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23 structure implies greater electrostatic interactions with the guest than those taking place
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25 with β -CD (-8.7 kcal/mol against -0.8 kcal/mol). Thus, experimental and theoretical
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27 data suggest that both steric complementarity and charge-transfer mechanisms are
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29 operating inside the cyclophane complex, whereas CD complex is mainly influenced by
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31 Van der Waals interactions. As a consequence, the total stabilisation energy is largely in
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33 favour of CBPQT⁴⁺ (-24.4 kcal/mol against -11.6 kcal/mol), which is in good qualitative
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35 agreement with the determined formation constants.
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44 **Materials and methods**

45 a) Chemicals

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53 Toluene and halogenobenzenes (Aldrich) were all of analytical reagent grade and were
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55 used as received. α -CD, β -CD and RAMEB were purchased from Wacker Chimie S.A.
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57 (Lyon). Cyclobis(paraquat-*p*-phenylene) was synthesised in our laboratory as described
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59 [6]. Tetrachloride salt of CBPQT⁴⁺ was used because of its greater solubility (~2mM)
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3 compared with tetrakis(hexafluorophosphate) salt (~0.01mM). Deionised water was
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5 used throughout this work.
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10 b) Static headspace
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15 Headspace sampling is employed with gas chromatography (GC) in numerous fields
16 and with a variety of applications [25, 26]. A headspace sample is in principle a gas
17 sample which has been previously in contact with a liquid or solid sample from which
18 volatile compounds were released into the gas with subsequent analysis by gas
19 chromatography. Headspace gas chromatography is therefore a technique of gas
20 extraction and can be carried out comparable to a solvent extraction as a one-step
21 extraction (static or equilibrium headspace) or as a continuous extraction (dynamic
22 headspace) [27]. Measurements were conducted with a Agilent headspace autosampler.
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24 Sample solutions of 5 mL containing various concentrations of pollutant (10-100 ppm)
25 were introduced into 10 mL headspace vials and sealed using silicone septa and
26 aluminium foil. The vials were then thermostated at $30 \pm 0.1^\circ\text{C}$. After the equilibrium
27 was established (30 min), 1 mL of vapor from the above solution was drawn out from
28 the vial using a gas-tight syringe and injected directly in the chromatographic column
29 via a transfer line. This sample was then analyzed by gas chromatography (Perkin Elmer
30 Autosystem XL) equipped with a flame-ionization detector using a DB624 column. The
31 GC settings were programmed as follows: detector temperature, 280°C ; column
32 temperature, 120°C during 8 min.
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55 Full equilibrium of the chemical solute between liquid and gas phases is required. For
56 the chemicals tested, the equilibrium time was 30 min. Linear response of the GC
57 detector to the chemical concentration range tested is another requirement for the
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successful application of the method. For all compounds, we verify that the GC detector responds linearly. The correlation coefficients are all better than 0.998.

c) Formation constants

The host/guest system (H/VOC) is characterised by a titration method. Different concentrations of host are used while the initial concentration of the VOC is constant. Assuming that 1:1 complexes are formed, the calculation of formation constant K_f is developed as follows:



$$K_f = [H/VOC]/[H][VOC] = [H/VOC]/([H]_T - [H/VOC]) * ([VOC]_T - [H/VOC]) \quad (2)$$

$$[H/VOC] = -1/2 \sqrt{[(1/K_f + [H]_T + [VOC]_T)^2 - 4[H]_T [VOC]_T]} + 1/2(1/K_f + [H]_T + [VOC]_T) \quad (3)$$

where K_f and T stand for formation constant and total, respectively. For a given value of K_f , $[H/VOC]$ is known. An algorithmic treatment developed in our laboratory is used to calculate the formation constant K_f from the experimental data [14]. Only one concentration of VOC in water is needed [7].

d) Molecular modeling

All the calculations were performed with CaChe [28]. Each symmetric host structure (CBPQT⁴⁺ and β -CD) was first subjected to an optimization with PM3 hamiltonian.

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3 Partial charges for both hosts and guest were then obtained from electrostatic potentials
4 with a single point calculation (B88-LYP energy functional with the DZVP basis sets).
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6 The docking of iodobenzene into each host was then realised by means of dummy
7 atoms, with the MM3 force field. The distance between host and guest and the rotation
8 of the guest inside the host were the two intermolecular variables investigated with a
9 regular increment (0.1Å for distance, 5° for rotation), the others being implicitly
10 submitted to Newton-Raphson optimisation. Complexation energy was defined as the
11 difference between energy of the optimal docked structure and energy of the individual
12 components.
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28 **Conclusion**

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31 This study explores for the first time the complexation ability of CBPQT⁴⁺ towards
32 aromatic VOCs. The theoretical and experimental results underlined a greater capacity
33 of CBPQT⁴⁺ to complex VOCs if compared with CDs due to a better encapsulation of
34 the phenyl ring by CBPQT⁴⁺. Nevertheless CDs, and especially modified CDs, present a
35 greater solubility than CBPQT⁴⁺. Further work in our laboratory will investigate the
36 capacity of CBPQT⁴⁺ as a molecular sensor for VOCs by cyclic voltamperometry.
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3 Figure Captions
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8 Figure 1: Chemical structure of (1) cyclobis(paraquat-*p*-phenylene) tetrachloride salt
9 and (2) α -CD: if $n=1$ and $R=H$; β -CD: if $n=2$ and $R = H$: RAMEB; if $n=2$ and $R = H$ or
10 CH_3 (1.8 OH groups modified per glucopyranose unit).
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17 Figure 2: Representation of the variation of the chromatogram of toluene 10 ppm (a)
18 with various concentrations of $CBPQT^{4+}$: 0.03mM (b), 0.1mM (c), 0.2mM (d) and
19 0.3mM (e).
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27 Figure 3: Representation of the experimental point (\blacklozenge) obtained for iodobenzene and
28 $CBPQT^{4+}$ compare with theoretical titration curve (- -) for a 1:1 complex ($K_f=9459 M^{-1}$)
29 with the algorithmic treatment.
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36 Figure 4: Variation of $\log K_f$ in function of molar refractivity (MR) of the substituent for
37 β -CD (\blacktriangle) and $CBPQT^{4+}$ (\blacklozenge).
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43 Figure 5: Optimized MM3 structures for inclusion of iodobenzene in $CBPQT^{4+}$ (1), and
44 in β -CD (2).
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3 Table Captions
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8 Table 1: Formation constants (M^{-1}) obtained at 30°C for the different VOCs with
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10 CBPQT⁴⁺, α -CD, β -CD and RAMEB
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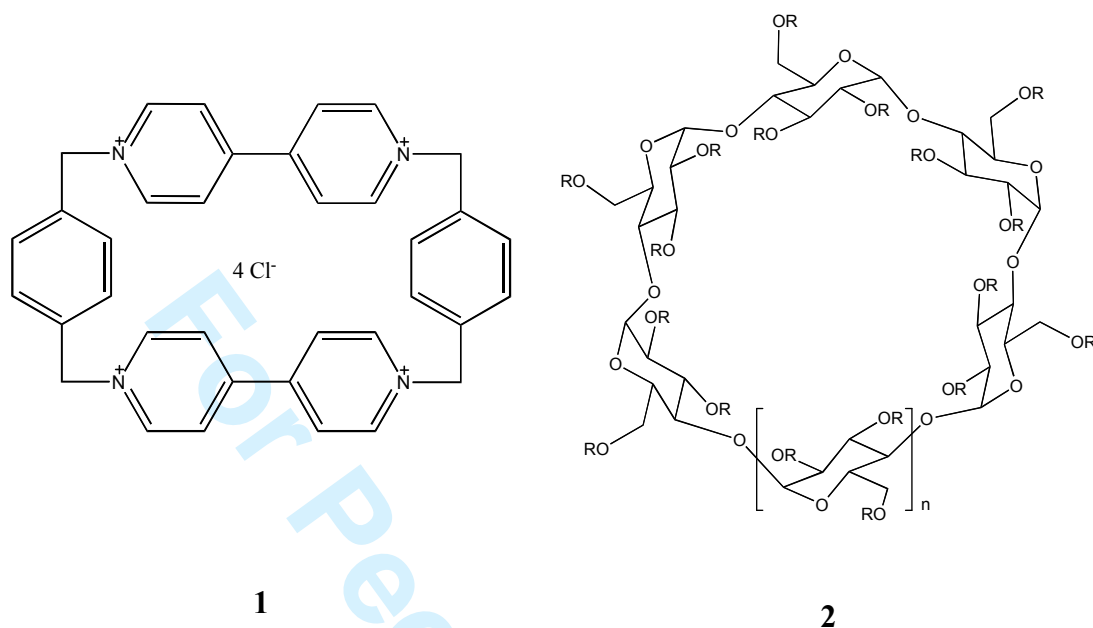


Figure 1: Chemical structure of (1) cyclobis(paraquat-*p*-phenylene) tetrachloride salt and (2) α -CD: if $n=1$ and $R=H$; β -CD: if $n=2$ and $R = H$; RAMEB; if $n=2$ and $R = H$ or CH_3 (1.8 OH groups modified per glucopyranose unit).

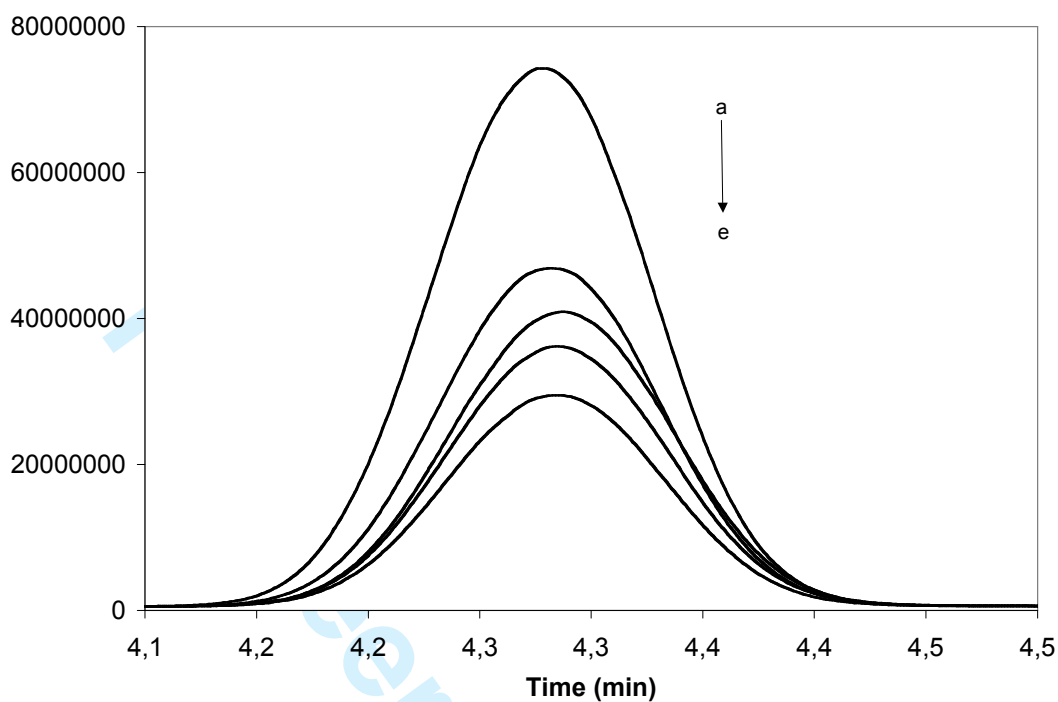


Figure 2: Representation of the variation of the chromatogram of toluene 10 ppm (a) with various concentrations of CBPQT⁴⁺: 0.03mM (b), 0.1mM (c), 0.2mM (d) and 0.3mM (e).

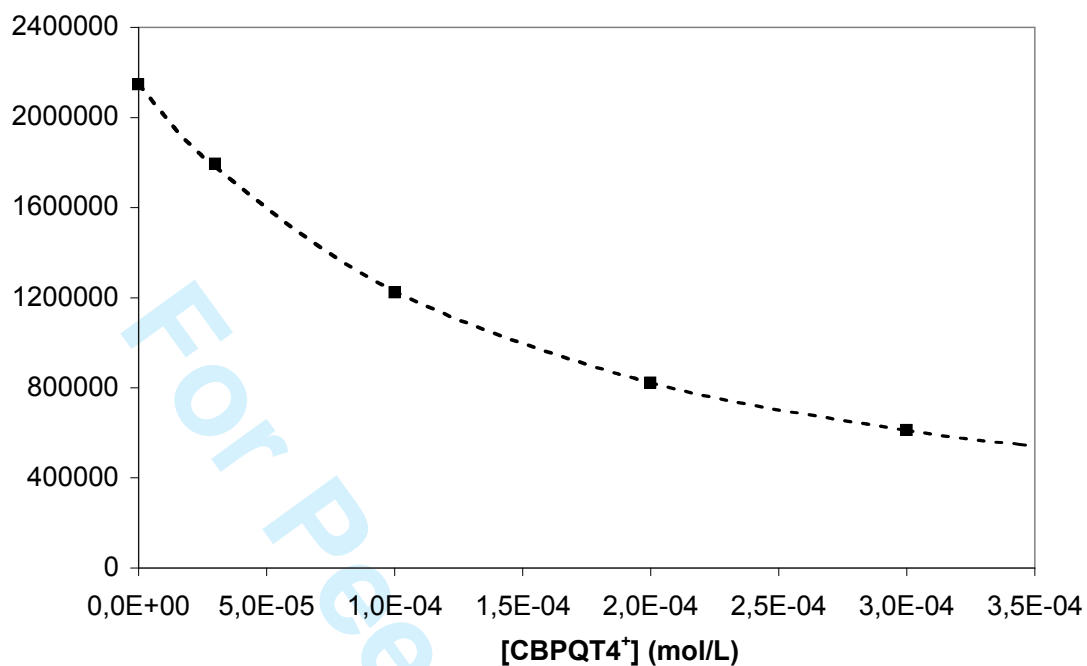


Figure 3: Representation of the experimental point (◆) obtained for iodobenzene and CBPQT⁴⁺ compare with theoretical titration curve (- -) for a 1:1 complex ($K_f=9459 \text{ M}^{-1}$) with the algorithmic treatment.

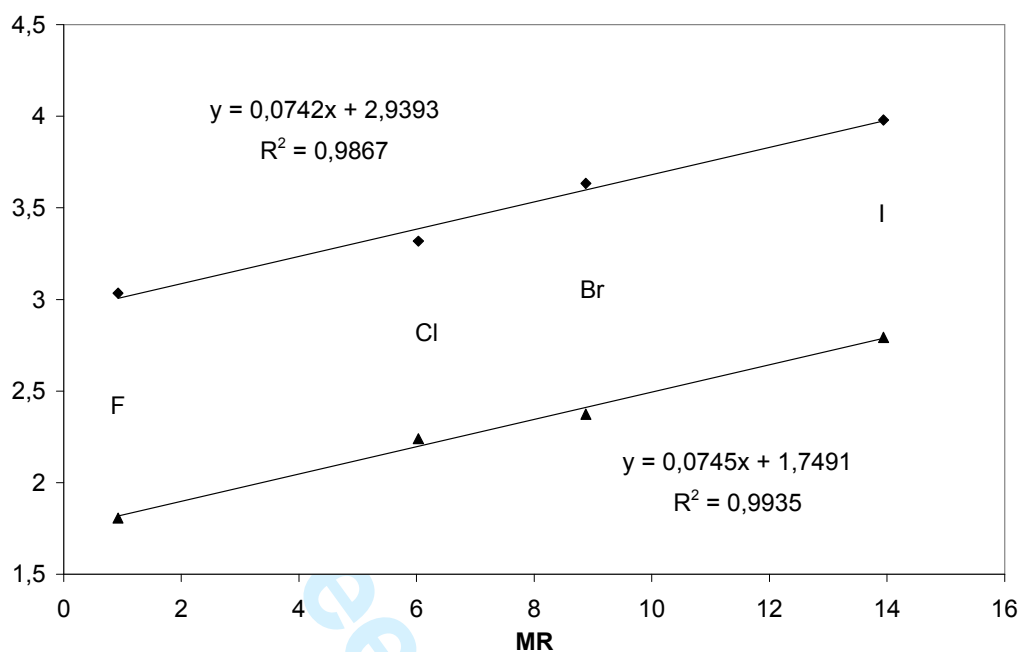


Figure 4: Variation of logK_f in function of molar refractivity (MR) of the substituent for β-CD (▲) and CBPQT⁴⁺ (◆).

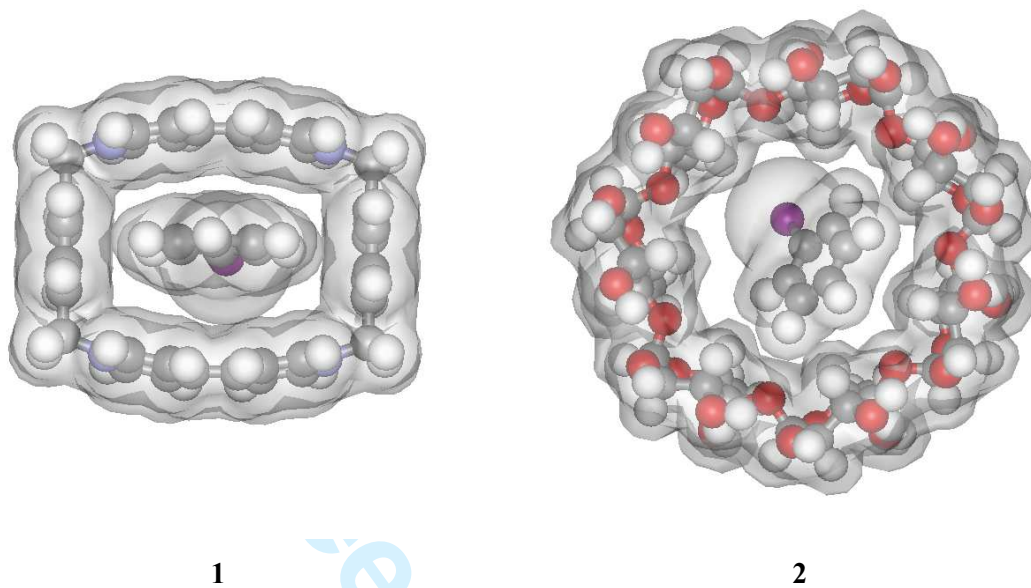
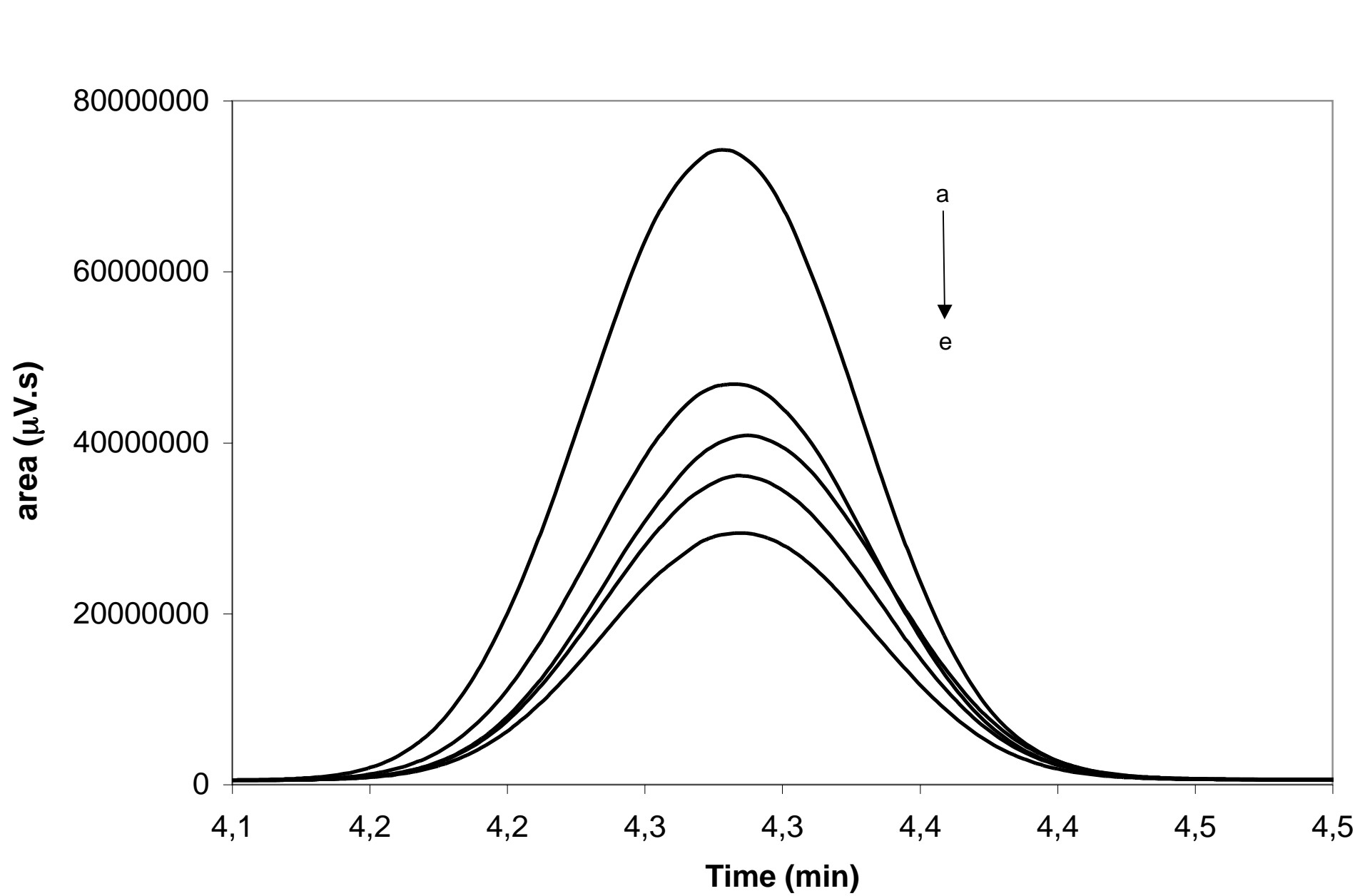


Figure 5: Optimized MM3 structures for inclusion of iodobenzene in CBPQT⁴⁺ (1), and in β -CD (2).

	CBPQT ⁴⁺	α -CD	β -CD	RAMEB
Toluene	3872	38 (29 ^a)	142 (140 ^b - 172 ^a)	171 (144 ^a)
Fluorobenzene	1083	31 (34 ^c)	64 (70 ^c)	90
Chlorobenzene	2300	128 (100 ^c)	174 (160 ^c)	157
Bromobenzene	4312	333 (51 ^c)	237 (310 ^c)	244
Iodobenzene	9459	917 (1100 ^c)	622 (800 ^c)	785

In bracket literature data; See references: ^a [13], ^b [11], ^c [12]

Table 1: Formation constants (M^{-1}) obtained at 30°C for the different VOCs with CBPQT⁴⁺, α -CD, β -CD and RAMEB



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