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Di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6: A "light fluorous" recyclable phase transfer catalyst

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A series of dibenzo-18-crown-6 lariat ethers containing two C_7H_{15} (**11**), $(CH_2)_2C_6F_{13}$ (**14**), $(CH_2)_2C_8F_{17}$ (**15**), NHC_7H_{15} (**18**) and $NHCH_2C_6F_{13}$ (**19**) sidearms were prepared and the single crystal X-ray structure of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**) is reported. The "light fluorous" dibenzo-18-crown-6 ether (**14**) has emerged as a stable and robust PTC catalyst, which can be recycled efficiently by fluorous solid-phase extraction, and gives better PTC catalytic activity compared to the parent, non-fluorinated PTC catalyst, dibenzo-18-crown-6, and the alkylated derivative (**11**) in aliphatic and aromatic nucleophilic substitutions.

1. Introduction

Since phase transfer catalysis can improve process efficiency, safety and reduce environmental impact, it is involved in more than 600 industrial applications and the commercial manufacture of billions of dollars worth of chemicals per year [1,2]. The role of a classical phase transfer catalyst (PTC) is to transfer an inorganic reagent from the non-organic phase (aqueous or solid) into the organic phase, thus enabling the organic substrate to react with the transferred anion and form the product in the organic phase reaction. The most difficult problem encountered in a phase transfer catalysed process is the separation of the organic product from the phase transfer catalyst. Quaternary ammonium salts, which are widely used in the pharmaceutical industry, are easily separated from the organic product by aqueous phase extraction or by extracting with dilute sodium hydroxide solution, but they are normally disposed of as aqueous waste. Polyethylene glycols can also be extracted easily into water, but there are environmental concerns about the waste disposal of such large amounts of phase transfer catalysts on a commercial scale every year. In order to make PTC catalysts more suitable for industrial applications, the PTC catalyst should be recovered and reused. Insoluble phase transfer catalysts are PTC catalysts that are bound to either an insoluble polymeric resin or an insoluble inorganic support. They were designed to offer easy recycling of the PTC catalyst with facile separation from the organic product, but the main disadvantages are that due to mass transfer problems the reactions are much slower compared to those using the analogous conventional soluble PTC catalysts and they are not mechanically robust enough to survive repeated reaction cycles on an industrial scale.

Fluorous chemistry has emerged recently as a powerful new separation technology for recycling catalysts and reagents that contain long perfluoroalkyl groups [3]. We, and others [4,5], are interested in harnessing these new separation strategies to design easily recyclable phase transfer catalysts (Fig. 1). Yasuda and Sakakura reported the first preparation of fluorous quaternary aliphatic phosphonium salts (**1**) which were used to catalyse the synthesis of propylene carbonate under supercritical carbon dioxide conditions and the spontaneous separation of the propylene carbonate enabled the successful recycling of the perfluoroalkylated catalyst under high carbon dioxide pressure and temperature [6]. We and Gladysz, and Horváth have also reported the syntheses of a series of heavily-fluorinated quaternary aliphatic phosphonium salts, whilst Ragogna has described the synthesis and characterisation of phosphonium ionic liquids that contain just one perfluoroalkyl group [7–9]. Gladysz [10] has demonstrated that the heavily-fluorinated phosphonium (**2**) and ammonium salts (**3**) act as phase transfer catalysts in nucleophilic substitution reactions of perfluoroalkyl halides under liquid–liquid conditions in a perfluoromethyldecalin/water biphase. The fluorous phosphonium salts were recovered by precipitation from the perfluorocarbon solvent with hexane, but after five recycles only 38% of the original catalyst mass remained and no recycling results were reported for the heavily-fluorinated ammonium salts. The first fluorous-derivatised chiral phase transfer catalyst (**4**) was applied successfully to the asymmetric synthesis of natural and

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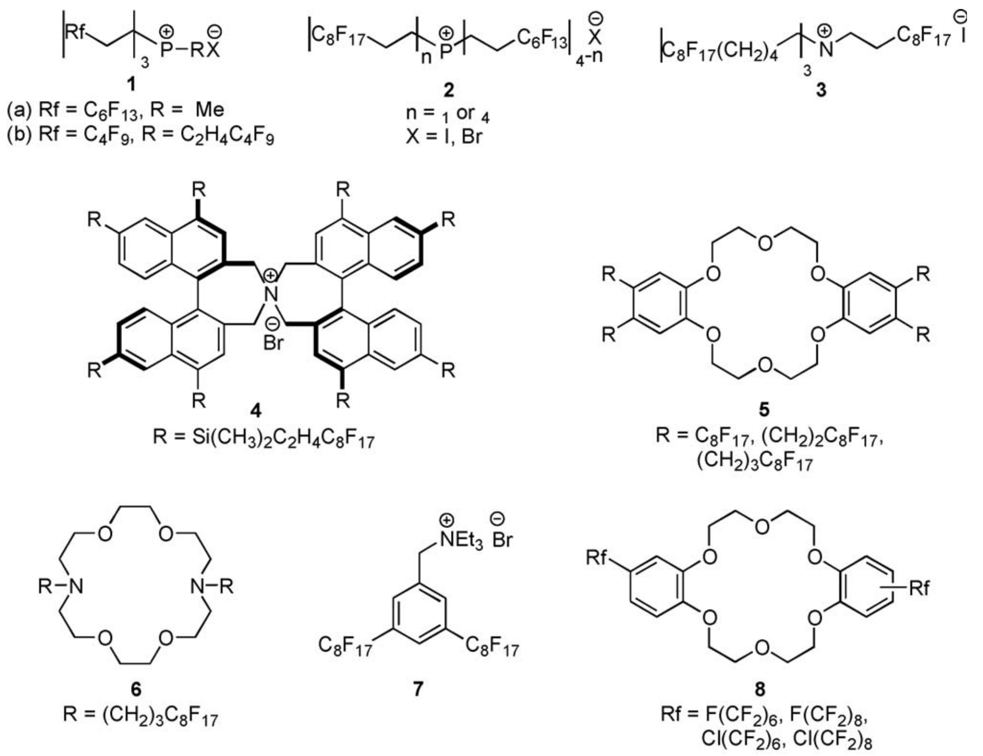


Fig. 1. Perfluoroalkylated phase transfer catalysts.

unnatural α-amino acids under liquid–liquid conditions (toluene/water) with high enantioselectivity (>90% ee) [11]. Since the chiral PTC catalyst (**4**) contained eight fluorous ponytails, it was recovered at the end of the reaction by extraction with perfluorohexane and was recycled three times without loss of reactivity or enantioselectivity. However, the catalytic activity of this "heavy fluorous" PTC was clearly reduced compared to the parent, non-fluorinated PTC due to its' low solubility in toluene. More recently, Pozzi reported the synthesis of a series of perfluorocarbon-soluble dibenzo-18-crown-6-ethers that contain four fluorous ponytails (**5**) [12]. Pozzi demonstrated for the first time that PTC catalysis could take place with organic substrates in a perfluorocarbon solvent and good catalytic activity and excellent recycling results were achieved over four cycles in a Finkelstein reaction between 1-bromooctane and potassium iodide in perfluoro-1,3-dimethylcyclohexane. The thermomorphic property of the "heavy fluorous" crown ether (**5c**; R = $(CH_2)_3C_8F_{17}$) was also exploited for the same benchmark reaction in toluene, but the results were not as impressive with a dramatic decrease in the catalytic activity and a less efficient recycling protocol.

We have been developing an alternative strategy in order to develop recyclable phase transfer catalysts. The aim of our work is to synthesise "light fluorous" PTC catalysts that can be used in conventional organic solvents and recycled by fluorous solid-phase extraction, thus avoiding the use of the expensive and environmentally-persistent perfluorocarbon solvents. The primary aim is to develop a stable and robust perfluoroalkylated PTC catalyst that can be used in a wide range of synthetic organic reactions, can be easily-recycled on fluorous reverse phase silica gel and possesses similar, if not better, catalytic activity compared to the parent, non-fluorinated PTC catalyst. In addition, the cost of the perfluoroalkylated PTC catalyst will be reduced by minimising the number of fluorous ponytails that are attached. This is a relatively underexplored area of fluorous PTC with just two reports in the literature. In 2007 we reported the synthesis of a perfluoroalkylated 4,13-diaza-18-crown-6 ether (**6**) that is an effective phase transfer catalyst under solid–liquid conditions in aliphatic and aromatic nucleophilic substitutions [13], whilst Pozzi [14] reported in 2009 that 3,5-bis(perfluorooctyl)benzyl-triethyl ammonium bromide (**7**) is an efficient solid–liquid phase transfer catalyst in epoxide ring opening and *N*-alkylations. Both of these PTCs can be reused without loss of activity over several reaction cycles. However, since the PTC catalytic activity of the perfluoroalkylated diaza-18-crown-6 ether (**6**) was much lower than the parent, non-fluorinated PTC catalyst, 4,13-diaza-18-crown-6, in the aliphatic nucleophilic substitution, we were interested in developing a more catalytically-active PTC using the same "light fluorous" approach. Since 18-crown-6-ethers are better PTC catalysts than diaza-18-crown-6-ethers, we decided to functionalise the aromatic rings of dibenzo-18-crown-6 ether with perfluoroalkyl and perfluoroalkylamino groups and in this paper we report the synthesis and catalytic applications of a small series of "light fluorous" dibenzo-18-crown-6-ethers [15]; work which was already in progress when Pozzi reported the syntheses of his "heavily-fluorinated" crown ethers [12].

A series of dibenzo-18-crown-6-ethers (**8**) containing perfluoroalkyl groups attached directly to the aromatic ring had been synthesised previously by the reaction of dibenzo-18-crown-6 with perfluoroalkanesulfinates in the presence of an oxidant, $Ce(SO_4)_2$ or $Mn(OAc)_3$ [16]. Potassium picrate extraction studies, however, had established that the complexing ability of these perfluoroalkylated crown ethers was decreased by the introduction of the perfluoroalkyl groups. We, therefore, decided that it was essential to introduce spacer groups between the perfluoroalkyl groups and the aromatic ring in order to minimise the electron-withdrawing effect of the perfluoroalkyl groups. Two different types of derivatised dibenzo-18-crown-6-ethers were prepared; the first type contained alkyl and perfluoroalkyl sidearms, whilst the second type contained alkylamino- and perfluoroalkylamino-substituents.

2. Results and discussion

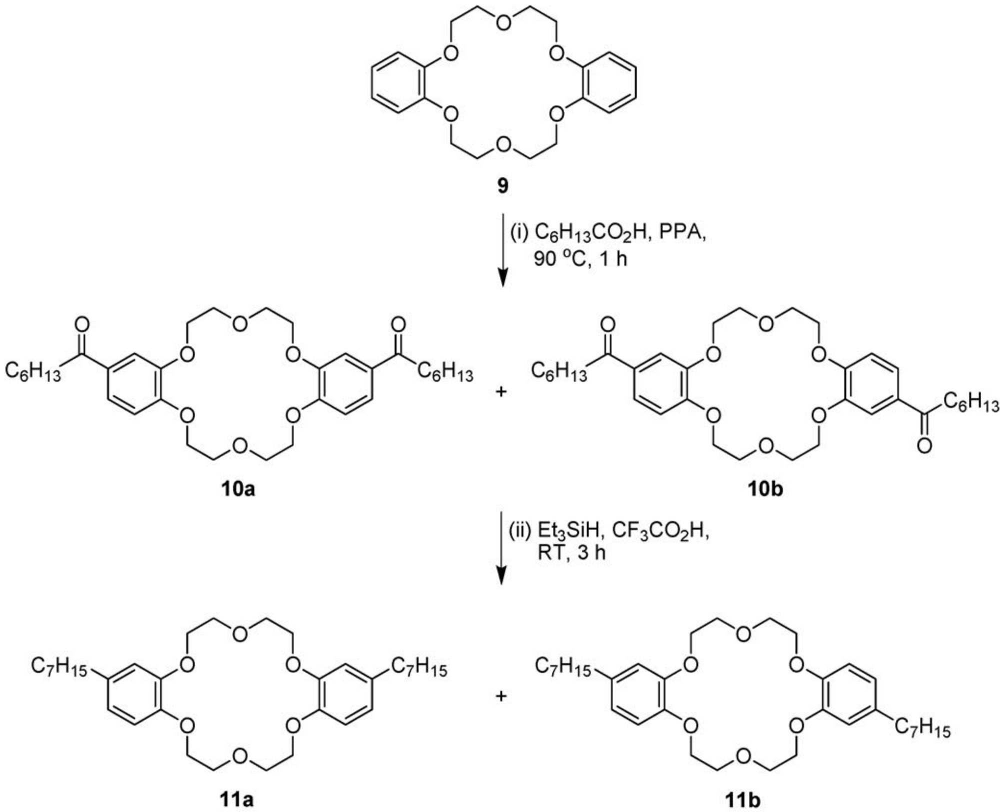
2.1. Synthesis of perfluoroalkylated dibenzo-18-crown-6-ethers

Diheptyl-dibenzo-18-crown-6 (**11**) was first synthesised, by a slightly modified procedure (Scheme 1), in order to have a direct comparison of the binding properties and catalytic activities of alkylated and perfluoroalkylated dibenzo-18-crown-6 ether derivatives. The first step involves the acylation of dibenzo-18-crown-6 with heptanoic acid using polyphosphoric acid (PPA) as the solvent and the catalyst. The two constitutional isomers, *cis*-4,4′-diheptanoyl-dibenzo-18-crown-6 (**10a**) and *trans*-4,5′-diheptanoyl-dibenzo-18-crown-6 (**10b**), were obtained in a high yield (84%) and were not separated. The carbonyl groups were reduced with triethylsilane in trifluoroacetic acid in the second step to give a mixture of the *cis*-4,4′- and *trans*-4,5′-diheptyl-dibenzo-18-crown-6-ethers, (**11a**) and (**11b**), respectively. Although diheptanoyl-dibenzo-18-crown-6 (**10**) is relatively insoluble in most common organic solvents, diheptyl-dibenzo-18-crown-6 (**11**) is much more soluble in solvents such as chloroform, tetrahydrofuran, ethyl acetate and diethyl ether. Diheptanoyl-dibenzo-18-crown-6 (**10**) had been prepared previously by acylation with heptanoic acid and Eaton's reagent (phosphoric acid in methanesulfonic acid), but this method lead to both acylation and glycol cleavage products [17]. A Raney nickel reduction of the ketone in cyclohexanol was then used to prepare diheptyl-dibenzo-18-crown-6 (**11**).

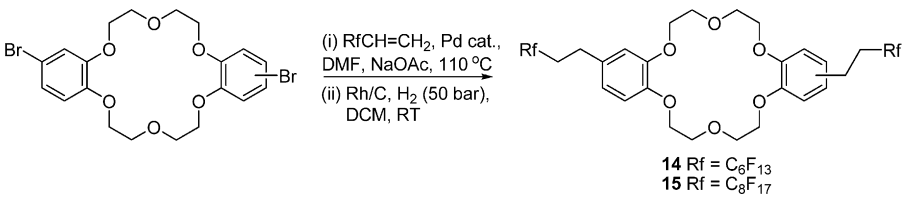
Initially, the synthesis of di(perfluoroalkyl)-dibenzo-18-crown-6 ether derivatives was attempted by an analogous approach by heating dibenzo-18-crown-6 with perfluoroheptanoic acid and polyphosphoric acid at 110 °C for 24 h. Although the reaction conditions were more aggressive than those used in the synthesis of the non-fluorous analogue, no reaction took place. Presumably, the strong electron-withdrawing effect of the perfluoroalkyl groups inhibited the formation of the active electrophilic species, $F_{13}CC{\equiv}O^{+}$. A similar result was also obtained with 2*H*,2*H*-perfluorooctanoic acid demonstrating that the methylene group did not insulate the reactive centre from the electron-withdrawing perfluoroalkyl group and so the reaction did not occur.

A completely different approach was, therefore, developed for the synthesis of the new perfluoroalkylated dibenzo-18-crown-6 ether derivatives containing the C_2H_4 insulating unit (Scheme 2). The fluorous ponytails were introduced by an efficient, palladium-catalysed Heck reaction [18] between dibromo-dibenzo-18-crown-6 and the appropriate 1*H*,1*H*,2*H*-perfluoroalkene to give the desired intermediates, (**12**) and (**13**), as a mixture of *cis*-4,4′- and *trans*-4,5′-isomers. The di(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)-dibenzo-18-crown-6 ether derivatives, (**14**) and (**15**), were then obtained in excellent yields by the subsequent reduction of the alkenes by a rhodium-catalysed hydrogenation. Significantly, these new dibenzo-18-crown-6 ether derivatives are soluble in most common organic solvents.

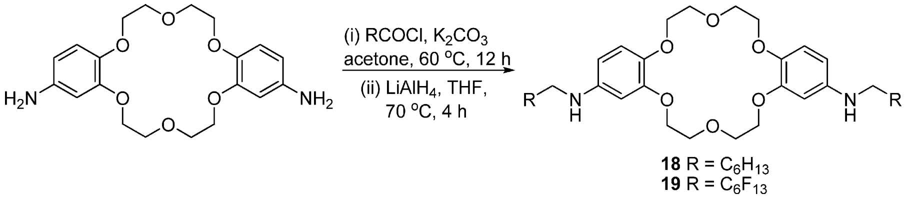
In the second strategy, in which the incorporation of a donor atom within the attached sidearm should provide the coordination centre of the crown ether with effective insulation from the electron-withdrawing effect of the fluorous ponytails, Scheme 3 outlines the two step synthesis of a new family of dialkylamino- and di(1*H*,1*H*-perfluoroalkylamino)-dibenzo-18-crown-6 ether derivatives by facile *N*-functionalisation of *cis*-4,4′-diamino-dibenzo-18-crown-6. The new dialkylamino-derivatives were synthesised here in order to have a direct comparison of the binding properties and catalytic activities of alkylated and perfluoroalkylated dibenzo-18-crown-6 ether derivatives. *Cis*-4,4′-diamino-dibenzo-18-crown-6 was reacted with either heptanoyl chloride or perfluoroheptanoyl chloride in the presence of potassium carbonate to give the amide derivatives, (**16**) and (**17**), which were then reduced with lithium aluminium hydride to give diheptylamino- and di(1*H*,1*H*-perfluoroheptylamino)-dibenzo-18-



Scheme 1. Synthesis of diheptyl-dibenzo-18-crown-6 (**11**).



Scheme 2. Synthesis of di(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)-dibenzo-18-crown-6-ethers.



Scheme 3. Synthesis of diheptylamino- and di(1*H*,1*H*-perfluoroheptylamino)-dibenzo-18-crown-6 ether derivatives.

crown-6 ether derivatives, (**18**) and (**19**). The advantage of the dialkylamino- and di(1*H*,1*H*-perfluoroalkylamino)-derivatives over the amide derivatives is that they are much more soluble in common organic solvents.

2.2. Structural study of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**)

The structure of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**) was determined by single crystal X-ray diffraction. In Fig. 2 the molecular structure shows that two methylene groups (C5 and C18) have rotated inwards. This conformation is characteristic of free crown ether ligands and has also been observed for dibenzo-18-crown-6 (**9**) [19]. Selected bond length data for (**15a**) are given in Table 1 and the average C*sp2*-O bond length (1.368(6) Å) is very similar to those obtained for dibenzo-18-crown-6 (1.362(11) Å) and *cis*-3,3′-dimethyldibenzo-18-crown-6 (1.372(4) Å) [19,20]. However, the dihedral angle between the mean planes of the aromatic rings is 71.6(2)° which is slightly larger than the dihedral angles observed for dibenzo-18-crown-6 (65.5(3)° and 66.1(3)°) and *cis*-3,3′-dimethyl-dibenzo-18-crown-6 (63.9(2)°) possibly due to the introduction of the fluorous ponytails. In previous structural determinations of perfluoroalkylated ligands and metal complexes [21], the fluorous ponytails normally radiate away from the ligand/metal centre and often demonstrate a strong preference for the long perfluoroalkyl

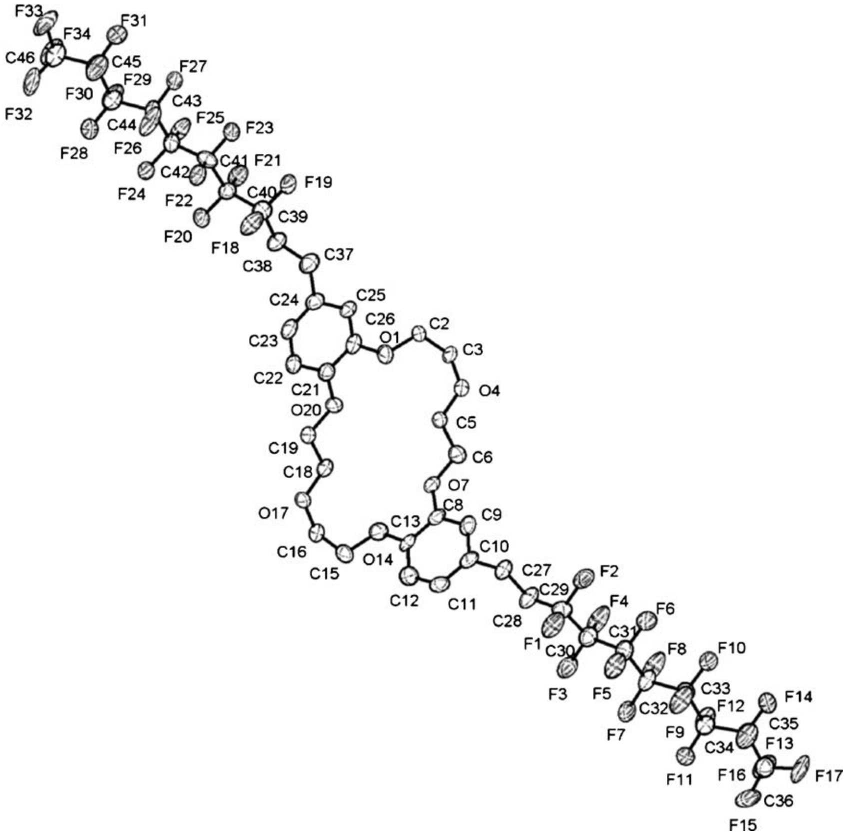


Fig. 2. The molecular structure of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**) showing 50% displacement ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) with estimated standard deviations (e.s.d.s.) in parentheses for (**15a**), *cis*-3,3′-dimethyldibenzo-18-crown-6 and dibenzo-18-crown-6.

	(**15a**)	3,3′-Dimethyl-DB18C6[a]	DB18C6[b]
O1–C26	1.384(6)	1.375(4)	1.369(11)
O7–C8	1.355(5)	1.369(4)	1.355(11)
O14–C13	1.375(6)	1.365(4)	1.355(12)
O20–C21	1.356(6)		1.368(11)
O1–C2	1.424(6)	1.435(5)	1.437(12)
O7–C6	1.421(6)	1.424(4)	1.452(12)
O14–C15	1.446(6)	1.426(4)	1.441(12)
O20–C19	1.407(6)		1.446(11)
O4–C3	1.410(5)	1.415(5)	1.420(12)
O4–C5	1.415(6)	1.416(5)	1.397(12)
O17–C16	1.399(6)		1.419(12)
O17–C18	1.404(5)		1.466(11)

[a] Data taken from Ref. [20].
[b] Data taken from Ref. [19].

Table 2
Sodium and potassium picrate extractions.

PTC	R	Picrate extracted (%)	
		Na^+	K^+
(**11**)	C_7H_{15}	9.1	25.6
(**14**)	$(CH_2)_2C_6F_{13}$	22.9	26.4
(**18**)	NHC_7H_{15}	23.4	24.4
(**19**)	$NHCH_2C_6F_{13}$	31.3	25.3

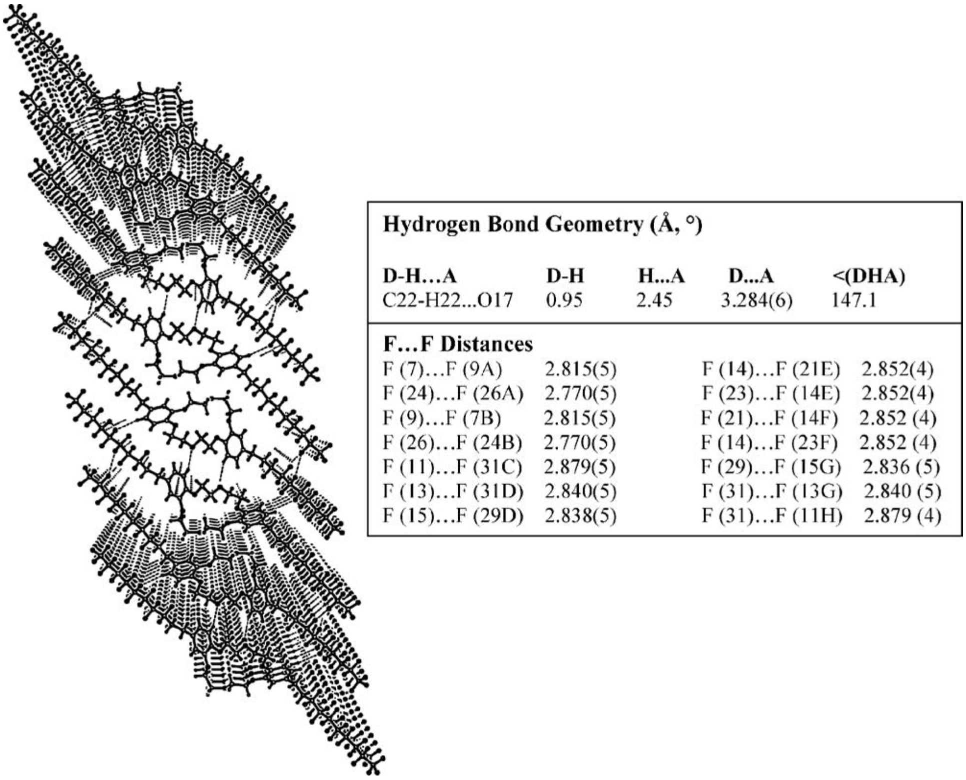
groups to align generating "fluorous domains" within the extended structures. The same phenomenons are observed here with the fluorous ponytails radiating linearly away from the macrocyclic ring and "fluorous domains" are observed in the extended structure of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**) resulting in a number of short F...F contacts with symmetry generated molecules (Fig. 3). Interestingly, there is also a weak intermolecular C–H...O interaction which may help to consolidate the crystal packing.

2.3. Picrate extraction studies

It is essential that the perfluoroalkylated dibenzo-18-crown-6 ether derivatives form stable complexes with metal ions in non-polar solvents in order to behave as efficient phase transfer catalysts. The picrate extraction technique is one of the most commonly used methods for assessing the cation binding strengths of crown ethers [22]. The ability of the alkylated and perfluoroalkylated dibenzo-18-crown-6 ether derivatives to coordinate to metal cations was investigated by carrying out sodium and potassium picrate extractions between dichloromethane and water. Since the four dibenzo-18-crown-6 ether derivatives have the same cavity-size, the results shown in Table 2 only illustrate the effect of the different substituents on the coordination centre of the macrocycle.

The binding ability of the dibenzo-18-crown-6 ether derivatives is dependent on the basicity of the ether oxygens and so, it should be directly related to the electron donating or electron-withdrawing effects of the substituents attached to the aromatic rings [23]. However, the percentage of potassium picrate extracted into the organic phase was independent of the type of substituent that was attached confirming that both the $ArCH_2CH_2$ and $ArNHCH_2$ spacer groups adequately insulate the ether oxygens from the electron-withdrawing effects of the perfluoroalkyl groups.

A very different trend was observed in the sodium picrate extraction studies. The amount of sodium picrate extracted into the organic phase was improved by the attachment of perfluoroalkyl groups with both types of sidearms: (**14**) ($R = CH_2CH_2C_6F_{13}$) > (**11**) ($R = C_7H_{15}$) and (**19**) ($R = NHCH_2C_6F_{13}$) > (**18**) ($R = NHC_7H_{15}$). The incorporation of amino substituents also increased the amount of



Hydrogen Bond Geometry (Å, °)

D-H…A	**D-H**	**H...A**	**D...A**	**<(DHA)**
C22-H22...O17	0.95	2.45	3.284(6)	147.1

F…F Distances

F (7)…F (9A)	2.815(5)	F (14)…F (21E)	2.852(4)
F (24)…F (26A)	2.770(5)	F (23)…F (14E)	2.852(4)
F (9)…F (7B)	2.815(5)	F (21)…F (14F)	2.852 (4)
F (26)…F (24B)	2.770(5)	F (14)…F (23F)	2.852 (4)
F (11)…F (31C)	2.879(5)	F (29)…F (15G)	2.836 (5)
F (13)…F (31D)	2.840(5)	F (31)…F (13G)	2.840 (5)
F (15)…F (29D)	2.838(5)	F (31)…F (11H)	2.879 (4)

Fig. 3. Extended structure of *cis*-4,4′-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15a**) showing short intermolecular interactions.

sodium picrate that was extracted into dichloromethane: (**18**) ($R = NHC_7H_{15}$) > (**11**) ($R = C_7H_{15}$) and (**19**) ($R = NHCH_2C_6F_{13}$) > (**14**) ($R = CH_2CH_2C_6F_{13}$). The results from the potassium picrate extraction studies demonstrate clearly that this is not an electronic effect for either the amino or the perfluoroalkyl sidearms. These substituents, however, could be inducing conformational changes in the polyether ring. In contrast to the potassium cation (2.66 Å), the smaller sodium ion does not interact simultaneously with all of the crown ether's oxygen atoms due to the pronounced difference in the diameters of the cation (1.99 Å) and the crown cavity (2.6–3.2 Å) [24]. Consequently, the distance between the sodium cation and the aromatic oxygens could be changing as a function of the nature of the substituents and hence, affecting the crown ether's binding abilities. Previous work has demonstrated that although dinitro-dibenzo-18-crown-6 binds Na^+ five times less effectively than the unsubstituted dibenzo-18-crown-6, the complexing properties of dibenzo-18-crown-6 and its' diamino derivative are almost identical in DMF [25]. This was attributed to conformational changes in the macrocyclic ring due to hydrogen-bonding interactions with the two amino groups.

2.4. Phase transfer catalysis and recycling studies

All of the functionalised dibenzo-18-crown-6 ether derivatives were evaluated as phase transfer catalysts in a simple aliphatic nucleophilic substitution under solid–liquid conditions (Eq. (1)) [26–28]. 1-Bromoctane was refluxed with an excess of potassium iodide in benzotrifluoride (BTF) in the presence of 2 mole% of crown ether and the reaction was monitored every hour by GC using biphenyl as an internal standard. In the absence of a crown ether there was no conversion to product. Fig. 4 and Table 3 demonstrate clearly that by adding perfluoroalkyl sidearms to the dibenzo-18-crown-6 structure in compounds (**14**) and (**15**), the phase transfer catalytic activity is increased significantly, but when alkyl sidearms are attached in compound (**11**), the catalytic activity only increases moderately compared to dibenzo-18-crown-6 (**9**). The results also showed that compounds (**14**) and (**15**) have essentially the same catalytic activity and so, the length of the perfluoroalkyl group does not affect the catalytic activity in benzotrifluoride. On the other hand, the *cis*-4,4′-dialkylamino crown ether (**18**) showed extremely poor catalytic activity under the same reaction conditions, whilst the *cis*-4,4′-di(1*H*,1*H*-perfluoroalkylamino)-derivatised crown ether (**19**) had a very similar rate profile to dibenzo-18-crown-6 after 5 h. Presumably, the polarity and solubility of (**18**) had an important effect on the reaction equilibria constants in benzotrifluoride and (**18**) may be a more efficient PTC catalyst in an alternative non-fluorinated organic solvent.

$$C_8H_{17}Br \xrightarrow[\text{BTF, 110 °C}]{\text{Rf-PTC (2 mole \%), KI (5 eq.)}} C_8H_{17}I \quad \text{(Equ 1)}$$

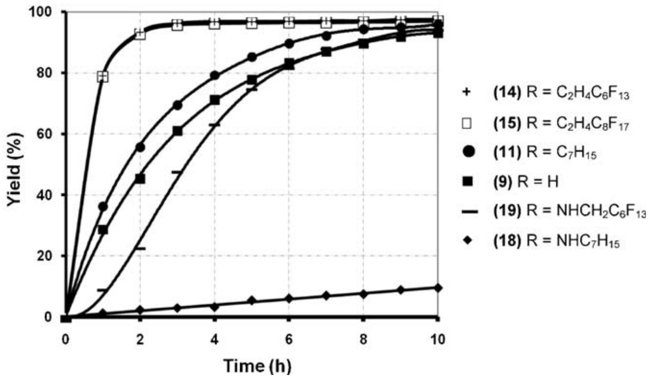


Fig. 4. Rate of formation of 1-iodooctane.

Table 3
Comparison of perfluoroalkylated PTC catalysts in Finkelstein-type reaction.

PTC	R	Time (h)	Yield (%)	TON[a]	TOF[b]
(**14**)	$(CH_2)_2C_6F_{13}$	3	96	48	16.0
(**15**)	$(CH_2)_2C_8F_{17}$	3	96	48	16.0
(**11**)	C_7H_{15}	6	90	45	7.5
(**9**)	H	6	83	42	6.9
(**5c**)[c]	$(CH_2)_3C_8F_{17}$	12	95	47	3.9
DA-18-C-6[d]	H	5	95	48	9.5
(**6**)[d]	$(CH_2)_3C_8F_{17}$	12	88	42	3.5

[a] TON = mmol of product/mmol catalyst.
[b] TOF = mmol of product/(mmol catalyst × hour).
[c] Results taken from Ref. [12].
[d] Results taken from Ref. [13].

The top section of Table 3 compares the PTC catalytic activity of the functionalised dibenzo-18-crown-6 ether derivatives with dibenzo-18-crown-6 (**9**) and Pozzi's perfluorocarbon-soluble dibenzo-18-crown-6 (**5c**) in the Finkelstein-type reaction between 1-bromooctane and potassium iodide in benzotrifluoride under identical conditions. The results for diaza-18-crown-6 (DA-18-C-6) and the "light fluorous" diaza-18-crown-6 ether derivative (**6**) in the same reaction under identical conditions are shown in the bottom section of Table 3. Out of the perfluoroalkylated PTC catalysts, macrocycles (**14**) and (**15**) are clearly the most catalytically-active PTC catalysts under these reaction conditions and the TOFs demonstrate that they are much more reactive than the parent, non-fluorinated PTC catalyst.

Two recycling protocols have been evaluated in this study. First, supported fluorous phase catalysis (SFPC) [29–31] was investigated for recycling the perfluoroalkylated dibenzo-18-crown-6 ether (**14**), which was immobilized on fluorous reverse phase silica gel (FRPSG) by simply refluxing in dichloromethane for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure giving the FRPSG-supported crown ether (**14**) as an air-stable, free-flowing powder.

Initially, when the reaction was carried out with the supported catalyst (**14**) in benzotrifluoride at 110 °C, the conversion was only 30% after 5 h. In comparison to the homogeneous reaction, which was complete after 3 h, this result demonstrated the reduced activity of the supported catalyst (**14**). The iodide displacement reaction was then carried out in ethyl acetate and THF in order to evaluate the effect of a different solvent environment on the reactivity of the supported catalyst. The results, shown in Fig. 5, established that the supported fluorous phase catalyst is more active in THF than in ethyl acetate or benzotrifluoride. One possible explanation is that the perfluoroalkylated crown ether (**14**) is more soluble in THF and so, it may come off the support allowing the reaction to occur homogeneously. Previous work has demonstrat-

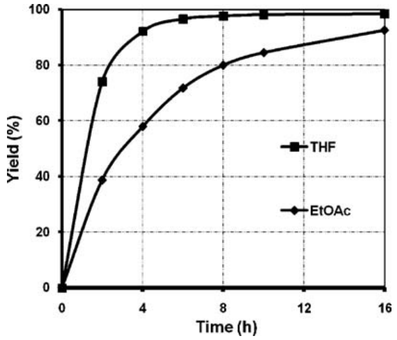


Fig. 5. Rate of formation of 1-iodooctane with supported catalyst (**14**).

Table 4
Recycling results for (**14**) supported on fluorous reverse phase silica gel.

$$C_8H_{17}Br \xrightarrow[\text{THF, 70 °C, 6 h}]{\text{FRPSG-}\mathbf{(14)}\text{ (2 mole \%), KI (5 eq.)}} C_8H_{17}I$$

.

Run	Supported catalyst used (mg)	Supported catalyst recovered (mg)[a]	Yield (%)
1	500	473 (94.6%)	95.2
2	473	445 (94.1%)	93.3
3	445	419 (94.2%)	90.0
4	419	392 (93.6%)	87.5

[a] Weight percent is shown in parentheses.

ed that by simply switching solvents, perfluoroalkylated catalysts can be driven onto or extracted off of the fluorous silica gel [32,33]. For example, Curran used dichloromethane as the reaction solvent in order to desorb a fluorous Grubbs–Hoveyda catalyst from the perfluoroalkylated silica support and hence, promote a high temperature metathesis reaction. At the end of the reaction a simple solvent switch to the polar, hydrophilic solvent, 80% MeOH/water, was used to re-attach the fluorous Grubbs–Hoveyda catalyst to the perfluoroalkylated solid support in order to enable its' recovery by filtration. Here, we have developed a similar controlled "release" and "capture" of the FRPSG-supported crown ether (**14**) in the reaction and work up respectively by using a simple solvent switch. After changing the solvent to hexane, the solid-supported catalyst was separated from the organic products by filtration and the solid was washed with cold water and then hexane, before being dried overnight under oil pump vacuum at 60 °C. In this way the supported catalyst (**14**) was reused in the aliphatic nucleophilic substitution four times (Table 4). After each cycle 94% of the perfluoroalkylated phase transfer catalyst was recovered and there was only a small drop in conversion. No catalyst leaching into the organic phase was detected either by ^{1}H or ^{19}F NMR spectroscopy.

The recycling of the perfluoroalkylated dibenzo-18-crown-6 ether (**14**) was also investigated using fluorous solid-phase extraction. After removing the potassium salts by filtration and by washing the organic phase with water, the crude reaction mixture was loaded onto a short column of fluorous reverse phase silica gel. Flash chromatography with benzotrifluoride gave the clean organic fraction, whilst the phase transfer catalyst was recovered essentially quantitatively (92–94%) by elution with trifluoroethanol. The recycling results are summarised in Table 5 and demonstrate that there was only a small drop in conversion (2%) over four cycles using the same short pad of FRP silica gel due to the mechanical losses of (**14**) after each recycle. The same phase transfer catalyst was also recycled four times on conventional silica gel using the same protocol, except that the catalyst was recovered with diethyl ether (see ESI). The recycling results were not as good as those using fluorous solid-phase extraction, with only 83–88% of the perfluoroalkylated phase transfer catalyst recovered in each cycle, such that only 55% of the original catalyst mass remained after four cycles.

The recovery of the non-fluorinated phase transfer catalysts, (**9**) and (**11**), was also investigated using both conventional and fluorous solid-phase extraction. Although clean organic products were obtained after the first step of the recycling using both methods, only 60% of dibenzo-18-crown-6 (**9**) was recovered. A similar low recovery was obtained with diheptyl-dibenzo-18-crown-6 (**11**) on fluorous reverse phase silica gel, but better results were obtained on conventional silica gel with 79–83% of the PTC catalyst recovered after each cycle (see ESI). However, this method is not efficient enough since only 50% of the original catalyst mass remained after only three runs.

The PTC catalytic applications of the alkylated and perfluoroalkylated dibenzo-18-crown-6 ether derivatives were also examined in the fluoride substitution of 2,4-dinitrochlorobenzene under solid–liquid conditions in acetonitrile at 85 °C with 1.5 equivalents of spray-dried potassium fluoride (Eq. (2)) [34]. This is a much more demanding reaction compared to the iodide displacement reaction (Eq. (1)) because it is much more difficult to transfer fluoride into organic solvents and iodide is a much better nucleophile than fluoride. By complexing to the potassium cation, the crown ethers not only increase the solubility and concentration of fluoride in acetonitrile, but they also increase the nucleophilicity of the fluoride ion. The reaction was monitored by GC after 2 and 12 h and the results are summarised in Fig. 6. Due to the low solubility of fluoride in acetonitrile [35], there was only 2% conversion to 2,4-dinitrofluorobenzene in the absence of a phase transfer catalyst after 12 h. In a similar way to the results from the iodide displacement reactions, the incorporation of a perfluoroalkyl group in the dibenzo-18-crown-6 structure gave the most efficient phase transfer catalyst (**14**), but in contrast to the earlier results, the alkylamino- and perfluoroalkylamino-derivatives, (**18**) and (**19**), were also better phase transfer catalysts than dibenzo-18-crown-6 (**9**) and the alkylated derivative (**11**). Not surprisingly, when the PTC catalyst loading was increased to 20 mol%, the rate of the aromatic nucleophilic substitution increased and the reaction was complete after just 6 h with dibenzo-18-crown-6 (**9**) and di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6 (**14**) giving yields of 95 and 98%, respectively.

After the fluorination of 2,4-dinitrochlorobenzene, the perfluoroalkylated phase transfer catalyst (**14**) was recycled by fluorous solid-phase extraction, which was the most efficient recycling technique developed for the same PTC catalyst in the iodide displacement reactions. The clean organic products were eluted first from the short column of fluorous reverse phase silica gel using dichloromethane. By a simple solvent switch to trifluoroethanol, the fluorinated dibenzo-18-crown-6 ether (**14**) was recovered quantitatively (93–95%) and excellent recycling

Table 5
Recycling results for (**14**) by fluorous solid-phase extraction.

$$C_8H_{17}Br \xrightarrow[\text{BTF, 110 °C, 5 h}]{\text{Rf-PTC }\mathbf{(14)}\text{ (2 mole \%), KI (5 eq.)}} C_8H_{17}I$$

.

Run	Catalyst used (mg)	Recovered catalyst (mg)[a]	Yield (%)
1	104	97 (93.3%)	91.8
2	97	91 (93.8%)	92.1
3	91	84 (92.3%)	90.5
4	84	79 (94.0%)	89.6

[a] Weight percent is shown in parentheses.

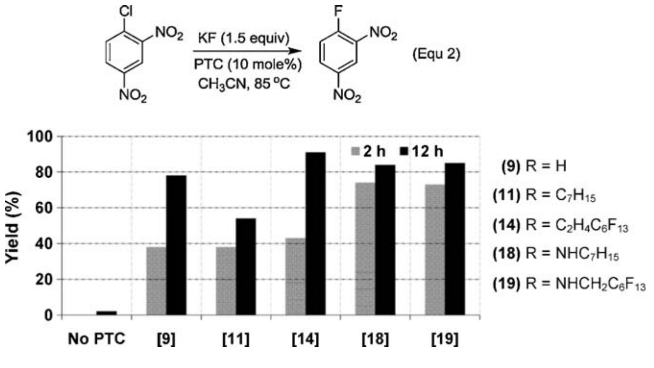
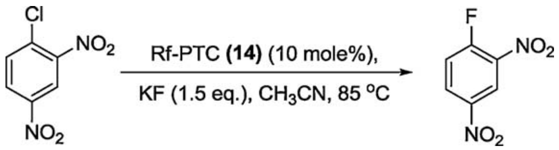


Fig. 6. Fluorination of 2,4-dinitrochlorobenzene.

Table 6
Recycling results for (**14**) by fluorous solid-phase extraction.



Run	Catalyst used (mg)	Recovered catalyst (mg)[a]	Yield (%)
1	106	101 (95.3%)	89.5
2	101	95 (94.1%)	86.8
3	95	89 (93.7%)	85.3
4	89	83 (93.3%)	83.5

[a] Weight percent is shown in parentheses.

results were obtained over four cycles on the same short column of FRP silica gel (Table 6). Since the *cis*-4,4′-diheptylamino- and *cis*-4,4′-di(1*H*,1*H*-perfluoroheptylamino)-crown ethers, (**18**) and (**19**), gave good results in the fluoride displacement reaction, the ability to recycle these crown ethers was also investigated by both conventional and fluorous solid-phase extraction. Unfortunately, the *cis*-4,4′-di(1*H*,1*H*-perfluoroheptylamino)-derivatised crown ether (**19**) could not be recovered efficiently by either method and only 80% of the *cis*-4,4′-diheptylamino-crown ether (**18**) was recovered from FRP silica gel.

3. Conclusions

Di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6 (**14**) was prepared as a mixture of *cis*-4,4′- and *trans*-4,5′-isomers in a two step synthesis from dibromo-dibenzo-18-crown-6 by a palladium-catalysed Heck reaction with 1*H*,1*H*,2*H*-perfluorooctene, followed by a rhodium-catalysed hydrogenation. Picrate extraction studies established that the perfluoroalkylated dibenzo-18-crown-6 ether derivative retained its' ability to coordinate to sodium and potassium ions demonstrating its' potential to be used as a phase transfer catalyst. Not only does the "light fluorous" macrocycle (**14**) give better PTC catalytic activity than dibenzo-18-crown-6 (**9**) in aliphatic and aromatic nucleophilic substitution reactions, but it can also be recycled efficiently by fluorous solid-phase extraction. In fact, di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6 (**14**) was recycled four times in the iodide displacement reaction of 1-bromooctane and four times in the fluoride displacement reaction of 2,4-dinitrochlorobenzene on the same short column of fluorous reverse phase silica gel without loss of activity. Excellent recycling results were also achieved in the iodide displacement reaction with the perfluoroalkylated dibenzo-18-crown-6 ether (**14**) supported on FRP silica gel.

4. Experimental

4.1. General experimental procedures

Proton, ^{19}F and ^{13}C NMR spectroscopies were carried out on a Bruker ARX 300 spectrometer at 300.14, 282.41 and 75.5 MHz, respectively. All chemical shifts are quoted in ppm using the high frequency positive convention; ^{1}H NMR spectra were referenced to external $SiMe_4$; ^{19}F NMR spectra to external $CFCl_3$ and ^{13}C NMR spectra to external $SiMe_4$. The highly coupled ^{13}C signals of the fluorinated carbons are not listed below. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. GC analyses were performed using a Perkin-Elmer Clarus 500 GC using a Perkin-Elmer-Elite Series PE-5 column (30 m × 0.25 mm, 5% diphenyl, 95% dimethyl polysiloxane). *Cis*-4,4′-diamino-dibenzo-18-crown-6, potassium picrate and sodium picrate were prepared by the literature methods [13,36–38]. Dibromo-dibenzo-18-crown-6 was purchased as a mixture of *cis*-4,4′ and *trans*-4,5′ isomers from Acros Organics and Fluoroflash® silica gel (40 μm) was purchased from Fluorous Technologies.

4.1.1. Diheptanoyl-dibenzo-18-crown-6 (**10**)

A slurry of heptanoic acid (4.2 g, 31.9 mmol) and dibenzo-18-crown-6 (5.0 g, 13.9 mmol) was added to polyphosphoric acid (25 mL, 51.3 g). The mechanically stirred (600 rpm) reaction mixture was heated for 1 h at 90 °C. The hot solution was then poured into a mechanically stirred ice-cold water bath (400 mL). After stirring for 4 h, the resulting pale yellow precipitate was filtered and recrystallised from EtOH (250 mL) to afford the pure product as a pale brown solid (6.8 g, 84%). The final product was isolated as a mixture of the *cis*-4,4′- and *trans*-4,5′-isomers. No attempt was made to separate these isomers. mp 118–120 °C (lit. [17], 119.5–122 °C); (Found: C, 69.99; H, 8.44. Calc. for $C_{34}H_{48}O_8$: C, 69.84; H, 8.27%); δ_H ($CDCl_3$) 7.48 (2H, dd, $^3J_{HH}$ 9.0, $^4J_{HH}$ 2.3, ArH), 7.41 (2H, d, $^4J_{HH}$ 2.3, ArH), 6.76 (2H, d, $^3J_{HH}$ 9.0, ArH), 4.12 (8H, m, $ArOCH_2$), 3.93 (8H, m, $ArOCH_2CH_2$), 2.82 (4H, t, $^3J_{HH}$ 7.5, $COCH_2$), 1.63 (4H, quintet, $^3J_{HH}$ 7.2, $COCH_2CH_2$), 1.25 (12H, m, 3 × CH_2), 0.81 (6H, t, $^3J_{HH}$ 6.4, CH_3); δ_C ($CDCl_3$) 199.3 (CO), 152.8 (C), 148.5 (C), 130.3 (C), 122.9 (CH), 111.9 (CH), 111.3 (CH), 69.8 (CH_2), 69.7 (CH_2), 68.6 (CH_2), 68.5 (CH_2), 38.2 (CH_2), 31.7 (CH_2), 29.1 (CH_2), 24.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3); *m*/*z* (FAB) 607 (MNa^+, 28%), 585.34260 ($C_{34}H_{48}O_8$ requires 585.34274), 499 (12), 233 (65), 163 (100).

4.1.2. Diheptyl-dibenzo-18-crown-6 (**11**)

Triethylsilane (4.9 g, 41.8 mmol) was added to a solution of diheptanoyl-dibenzo-18-crown-6 (5.0 g, 8.6 mmol) in trifluoroacetic acid (60 mL). The solution was stirred at room temperature for 3 h under an inert atmosphere. The reaction mixture was then diluted with chloroform (75 mL). An aqueous solution of sodium hydrogen carbonate was added slowly until no further exothermicity was observed. The organic phase was separated, washed with water (2 × 75 mL) and dried over magnesium sulfate. The solvent was removed and the resulting yellow solid was recrystallised from ethanol to give the desired product as a pale brown powder (1.9 g, 40%). mp 84–86 °C (lit. [17], 89–91 °C); (Found: C, 73.41; H, 9.25. Calc. for $C_{34}H_{52}O_6$: C, 73.35; H, 9.41%); δ_H ($CDCl_3$) 6.70 (2H, dd, $^3J_{HH}$ 8.6, $^4J_{HH}$ 2.3, ArH), 6.62 (2H, d, $^3J_{HH}$ 8.6, ArH), 6.59 (2H, d, $^4J_{HH}$ 2.3, ArH), 4.07 (8H, m, $ArOCH_2$), 3.94 (8H, m, $ArOCH_2CH_2$), 2.44 (4H, t, $^3J_{HH}$ 7.6, $ArCH_2$), 1.48 (4H, quintet, $^3J_{HH}$ 7.0, $ArCH_2CH_2$), 1.21 (16H, m, 4 × CH_2), 0.80 (6H, t, $^3J_{HH}$ 6.7, CH_3); δ_C ($CDCl_3$) 148.6 (C), 146.8 (C), 136.2 (C), 120.8 (CH), 114.2 (CH), 113.8 (CH), 70.0 (CH_2), 69.1 (CH_2), 68.9 (CH_2), 35.5 (CH_2), 31.8 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3); *m*/*z* (FAB) 556.37624 ($C_{34}H_{52}O_6$ requires 556.37639), 219 (45%), 149 (100).

4.1.3. General procedure for synthesis of di(1H,2H-perfluoro-1-alkenyl)-dibenzo-18-crown-6-ethers

A suspension of dibromo-dibenzo-18-crown-6 (0.5 g, 1.0 mmol), the appropriate 1*H*,1*H*,2*H*-perfluoro-1-alkene (4.0 mmol), *trans*-di-*m*-acetatobis[2-(di-*o*-tolylphosphino) benzyl]dipalladium (II), Herrmann's catalyst (30 mg, 0.03 mmol) and sodium acetate (250 mg, 3.0 mmol) in wet *N*,*N*′-dimethylformamide (2 mL of water in 30 mL of *N*,*N*′-dimethylformamide) was stirred under an inert atmosphere at 120 °C for 72 h. After cooling to room temperature, the solvent was eliminated under reduced pressure and the resulting solid was partitioned between dichloromethane (40 mL) and water (40 mL). The organic layer was washed with water (40 mL) and brine (40 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure.

*4.1.3.1. Di(1H,2H-perfluoro-1-octenyl)-dibenzo-18-crown-6 (**12**).*

The resulting pale yellow solid was recrystallised from ethanol to give the desired product as a white solid (0.9 g, 84%). mp 100–102 °C; (Found: C, 41.16; H, 2.42. Calc. for $C_{36}H_{26}F_{26}O_6$: C, 41.24; H, 2.50%); δ_H (CDCl$_3$) 7.02 (2H, dt, $^3J_{HH}$ 16.0, $^4J_{HF}$ 2.0, ArC*H*=CHCF$_2$), 6.95 (2H, dd, $^3J_{HH}$ 8.1, $^4J_{HH}$ 2.0, ArH), 6.89 (2H, d, $^4J_{HH}$ 1.8, ArH), 6.78 (2H, d, $^3J_{HH}$ 8.1, ArH), 5.95 (2H, dt, $^3J_{HH}$ 16.0, $^3J_{HF}$ 12.3, ArH=C*H*CF$_2$), 4.12 (8H, m, ArOCH$_2$), 3.96 (8H, m, ArOCH$_2$C*H*$_2$); δ_F (CDCl$_3$) −80.77 (3F, t, $^4J_{FF}$ 9.9, CF$_3$), −110.48 (2F, t, $^4J_{FF}$ 12.2, ArCH=CHCF$_2$), −121.57 (2F, m, CF$_2$), −122.84 (2F, m, CF$_2$), −123.07 (2F, m, CF$_2$), −126.12 (2F, m, CF$_2$); δ_C (CDCl$_3$) 150.7 (C), 148.9 (C), 139.4 (t, $^2J_{CF}$ 9.8, CH), 126.7 (C), 122.1 (CH), 112.8 (CH), 112.0 (CH), 111.8 (CH), 69.8 (CH$_2$), 69.7 (CH$_2$), 68.9 (CH$_2$), 68.6 (CH$_2$); *m*/*z* (FAB) 1087 (MK$^+$, 30%), 1071 (MNa$^+$, 22), 1048 (M$^+$, 45).

*4.1.3.2. Di(1H,2H-perfluoro-1-decenyl)-dibenzo-18-crown-6 (**13**).*

After removing the DMF, the resulting solid was partitioned between dichloromethane-ethyl acetate (20–20 mL) and water (40 mL) and the normal work up procedure was followed. The resulting yellow solid was recrystallised from ethanol to give the desired product as a white solid (0.5 g, 40%). mp 130–132 °C; (Found: C, 38.61; H, 2.01. Calc. for $C_{40}H_{26}F_{34}O_6$: C, 38.48; H, 2.10%); δ_H (CDCl$_3$) 7.02 (2H, dt, $^3J_{HH}$ 16.2, $^4J_{HF}$ 2.1, ArC*H*=CHCF$_2$), 6.97 (2H, dd, $^3J_{HH}$ 8.2, $^4J_{HH}$ 2.0, ArH), 6.89 (2H, d, $^4J_{HH}$ 2.0, ArH), 6.74 (2H, d, $^3J_{HH}$ 8.2, ArH), 5.95 (2H, dt, $^3J_{HH}$ 16.2, $^3J_{HF}$ 12.0, ArCH=C*H*CF$_2$), 4.12 (8H, m, ArOCH$_2$), 3.97 (8H, m, ArOCH$_2$C*H*$_2$); δ_F (CDCl$_3$) −80.71 (3F, t, $^4J_{FF}$ 10.0, CF$_3$), −110.43 (2F, t, $^4J_{FF}$ 12.6, ArCH=CHCF$_2$), −121.33 (2F, m, CF$_2$), −121.84 (4F, m, 2 × CF$_2$), −122.65 (2F, m, CF$_2$), −123.01 (2F, m, CF$_2$), −126.04 (2F, m, CF$_2$); δ_C (CDCl$_3$) 150.7 (C), 148.9 (C), 139.4 (t, $^2J_{CF}$ 9.5, CH), 126.8 (C), 122.1 (CH), 112.9 (CH), 111.9 (CH), 111.8 (CH), 69.9 (CH$_2$), 69.8 (CH$_2$), 68.9 (CH$_2$), 68.6 (CH$_2$); *m*/*z* (FAB) 1287 (MK$^+$, 70%), 1271 (MNa$^+$, 100).

4.1.4. General procedure for synthesis of di(1H,1H,2H,2H-perfluoroalkyl)-dibenzo-18-crown-6-ethers

The appropriate di(1*H*,2*H*-perfluoro-1-alkenyl)-dibenzo-18-crown-6 (0.48 mmol), 5% rhodium on charcoal (20 mg) and dichloromethane (25 mL) were stirred in a hydrogenation apparatus at 50 bar hydrogen pressure at room temperature for 48 h. The organic phase was filtered through celite and the solvent was removed under reduced pressure.

*4.1.4.1. Di(1H,1H,2H,2H-perfluorooctyl)-dibenzo-18-crown-6 (**14**).*

Recrystallisation from ethanol gave the desired product as a white solid (0.4 g, 79%). mp 118–120 °C; (Found: C, 41.13; H, 2.78. Calc. for $C_{36}H_{30}F_{26}O_6$: C, 41.08; H, 2.87%); δ_H (CDCl$_3$) 6.74 (2H, d, $^3J_{HH}$ 8.2, ArH), 6.67 (4H, m, ArH), 4.09 (8H, m, ArOCH$_2$), 3.95 (8H, m, ArOCH$_2$C*H*$_2$), 2.76 (4H, m, ArCH$_2$), 2.26 (4H, m, CH$_2$CF$_2$); δ_F (CDCl$_3$) −80.74 (3F, t, $^4J_{FF}$ 9.5, CF$_3$), −114.60 (2F, t, $^4J_{FF}$ 14.6, CH$_2$CF$_2$), −121.85 (2F, m, CF$_2$), −122.80 (2F, m, CF$_2$), −123.47 (2F, m, CF$_2$), −126.08 (2F, m, CF$_2$); δ_C (CDCl$_3$) 148.9 (C), 147.5 (C), 132.1 (C), 120.7 (CH), 113.7 (2 × CH), 69.9 (CH$_2$), 68.9 (CH$_2$), 33.2 (t, $^2J_{CF}$ 22.6, CH$_2$), 26.0 (CH$_2$); *m*/*z* (FAB) 1091 (MK$^+$, 35%), 1075 (MNa$^+$, 30), 1052 (M$^+$, 22).

*4.1.4.2. Di(1H,1H,2H,2H-perfluorodecyl)-dibenzo-18-crown-6 (**15**).*

The same protocol was followed using di(1*H*,2*H*-perfluoro-1-decenyl)-dibenzo-18-crown-6 (1.0 g, 0.8 mmol), 5% rhodium on charcoal (20 mg) and dichloromethane (25 mL). Recrystallisation from ethanol gave the desired product as a white solid (0.8 g, 80%). mp 136–138 °C; (Found: C, 38.51; H, 2.36. Calc. for $C_{40}H_{30}F_{34}O_6$: C, 38.36; H, 2.41%); δ_H (CDCl$_3$) 6.75 (2H, d, $^3J_{HH}$ 7.9, ArH), 6.67 (4H, m, ArH), 4.09 (8H, m, ArOCH$_2$), 3.96 (8H, m, ArOCH$_2$C*H*$_2$), 2.76 (4H, m, ArCH$_2$), 2.25 (4H, m, CH$_2$CF$_2$); δ_F (CDCl$_3$) −80.71 (3F, t, $^4J_{FF}$ 9.5, CF$_3$), −114.55 (2F, t, $^4J_{FF}$ 15.2, CH$_2$CF$_2$), −121.77 (6F, m, 3 × CF$_2$), −122.65 (2F, m, CF$_2$), −123.42 (2F, m, CF$_2$), −126.04 (2F, m, CF$_2$); δ_C (CDCl$_3$) 148.9 (C), 147.5 (C), 132.2 (C), 120.8 (CH), 114.0 (CH), 113.6 (CH), 70.0 (CH$_2$), 69.1 (CH$_2$), 33.6 (t, $^2J_{CF}$ 22.4, CH$_2$), 26.0 (CH$_2$); *m*/*z* (FAB) 1291 (MK$^+$, 90%), 1275 (MNa$^+$, 100), 1252 (M$^+$, 12).

*4.1.5. Cis-4,4′-diheptylamido-dibenzo-18-crown-6 (**16**)*

A solution of heptanoyl chloride (0.5 g, 3.1 mmol) in acetone (10 mL) was added to a solution of *cis*-4,4′-diamino-dibenzo-18-crown-6 (0.5 g, 1.3 mmol) in acetone (40 mL). The mixture was stirred for 2 h at room temperature and for a further 12 h at 60 °C. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting solid was dissolved in trifluoroethanol (40 mL), and water (40 mL) was added to the solution. The mixture was stirred for 1 h at −5 °C. The resulting precipitate was filtered and the solid was recrystallised from ethanol to afford a pale red solid (0.4 g, 47%). mp 192–194 °C; (Found: C, 66.36; H, 8.16; N, 4.42. Calc. for $C_{34}H_{50}N_2O_8$: C, 66.43; H, 8.20; N, 4.56%); δ_H (DMSO-d$_6$) 9.70 (2H, br s, NHCO), 7.36 (2H, d, $^4J_{HH}$ 2.4, ArH), 7.09 (2H, dd, $^3J_{HH}$ 9.0, $^4J_{HH}$ 2.4, ArH), 6.88 (2H, d, $^3J_{HH}$ 9.0, ArH), 4.06 (8H, m, ArOCH$_2$), 3.87 (8H, m, ArOCH$_2$C*H*$_2$), 2.26 (4H, t, $^3J_{HH}$ 7.3, NHCOC*H*$_2$), 1.56 (4H, quintet, $^3J_{HH}$ 6.4, COCH$_2$C*H*$_2$), 1.27 (12H, s, 3 × CH$_2$), 0.86 (6H, t, $^3J_{HH}$ 6.7, CH$_3$); δ_C (DMSO-d$_6$) 170.7 (CO), 147.6 (C), 143.7 (C), 133.0 (C), 112.6 (CH), 110.9 (CH), 104.8 (CH), 68.9 (CH$_2$), 68.8 (CH$_2$), 67.9 (CH$_2$), 67.6 (CH$_2$), 36.3 (CH$_2$), 31.0 (CH$_2$), 28.3 (CH$_2$), 25.1 (CH$_2$), 22.0 (CH$_2$), 13.9 (CH$_3$); *m*/*z* (FAB) 653 (MK$^+$, 8%), 614.35679 ($C_{34}H_{50}N_2O_8$ requires 614.35672, 100), 503 (12).

*4.1.6. Cis-4,4′-di(perfluoroheptylamido)-dibenzo-18-crown-6 (**17**)*

A mixture of perfluoroheptanoyl chloride (4.8 g, 12.6 mmol), *cis*-4,4′-diamino-dibenzo-18-crown-6 (2.1 g, 5.3 mmol) and potassium carbonate (2.0 g, 14.5 mmol) in acetone (40 mL) was stirred at room temperature for 2 h. The reaction mixture was then heated at 60 °C for 12 h. After cooling to room temperature, the solvent was eliminated under reduced pressure. The resulting solid was stirred in trifluoroethanol–water (75:75 mL) at room temperature for 1 h. The precipitate was filtered and recrystallised from trifluoroethanol to afford a pale brown solid (0.5 g, 23%). mp 220–222 °C; (Found: C, 37.74; H, 2.18; N, 2.69. Calc. for $C_{34}H_{24}F_{26}N_2O_8$: C, 37.72; H, 2.23; N, 2.59%); δ_H (DMSO-d$_6$) 11.02 (2H, br s, NHCO), 7.33 (2H, d, $^4J_{HH}$ 2.3, ArH), 7.30 (2H, dd, $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.3, ArH), 7.01 (2H, d, $^3J_{HH}$ 8.8, ArH), 4.12 (8H, m, ArOCH$_2$), 3.90 (8H, m, ArOCH$_2$C*H*$_2$); δ_F (DMSO-d$_6$) −80.17 (3F, t, $^4J_{FF}$ 9.7, CF$_3$), −117.87 (2F, t, $^4J_{FF}$ 14.2, NHCOCF$_2$), −121.50 (2F, m, CF$_2$), −121.98 (2F, m, CF$_2$), −122.49 (2F, m, CF$_2$), −125.67 (2F, m, CF$_2$); δ_C (DMSO-d$_6$) 155.2 (t, $^2J_{CF}$ 22.7, CO), 148.5 (C), 146.7 (C), 130.1 (C), 114.4 (CH), 113.7 (CH), 108.0 (CH), 69.5 (CH$_2$), 69.4 (CH$_2$), 68.8 (CH$_2$), 68.7 (CH$_2$); *m*/*z* (FAB) 1121 (MK$^+$, 88%), 1105 (MNa$^+$, 90), 1083 (MH$^+$, 8%).

*4.1.7. Cis-4,4′-di(heptylamino)-dibenzo-18-crown-6 (**18**)*

Cis-4,4′-Di(heptylamido)-dibenzo-18-crown-6 (0.5 g, 0.8 mmol) and lithium aluminium hydride (0.4 g, 10.4 mmol) were dissolved in dry tetrahydrofuran (20 mL). The suspension was heated for 4 h at 70 °C under an inert atmosphere. After cooling to room temperature, water was added carefully until no reaction occurred. The mixture was filtered and the filtrate was washed with hot diethyl ether. The aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with water (2 × 20 mL), and dried over magnesium sulfate. The solid was recrystallised from diethyl ether to afford a pale brown solid (0.25 g, 50%). mp 122–124 °C; (Found: C, 69.51; H, 9.19; N, 4.68. Calc. for $C_{34}H_{54}N_2O_6$: C, 69.59; H, 9.28; N, 4.77%); δ_H (CDCl$_3$) 6.69 (2H, d, $^3J_{HH}$ 8.6, ArH), 6.53 (2H, d, $^4J_{HH}$ 2.6, ArH), 6.07 (2H, dd, $^3J_{HH}$ 8.6, $^4J_{HH}$ 2.6, ArH), 4.04 (8H, m, ArOCH$_2$), 3.91 (8H, m, ArOCH$_2$CH$_2$), 3.28 (2H, br s, NH), 2.96 (4H, t, $^3J_{HH}$ 7.1, NHC*H*$_2$), 1.52 (4H, quintet, $^3J_{HH}$ 7.2, NHCH$_2$C*H*$_2$), 1.23 (16H, m, 4 × CH$_2$), 0.81 (6H, t, $^3J_{HH}$ 6.7, CH$_3$); δ_C (CDCl$_3$) 150.4 (C), 144.1 (C), 140.9 (C), 117.2 (CH), 104.7 (CH), 100.6 (CH), 70.6 (CH$_2$), 70.3 (CH$_2$), 69.9 (CH_2), 68.8 (CH_2), 44.9 (CH_2), 31.8 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 27.2 (CH_2), 22.6 (CH_2), 14.1 (CH_3); m/z (FAB) 587.40600 ($C_{34}H_{55}N_2O_6$ requires 587.40601).

4.1.8. *Cis-4,4′-di(1H,1H-perfluoroheptylamino)-dibenzo-18-crown-6 (**19**)*

A solution of lithium aluminium hydride (120 mg, 3.0 mmol) in dry tetrahydrofuran (10 mL) was added dropwise to *cis*-4,4′-di(perfluoroheptylamido)-dibenzo-18-crown-6 (250 mg, 0.2 mmol) stirring in dry tetrahydrofuran (10 mL) at room temperature under an inert atmosphere. The reaction mixture was then heated to 70 °C for 4 h. After cooling to room temperature, water (2 mL) was added dropwise and then sulfuric acid (4 mL, 6 M) was added until everything dissolved. The resulting solution was extracted with dichloromethane (3 × 30 mL). The extracts were combined, washed with sodium thiosulfate (30 mL, 0.1 M) and then with water (30 mL). The organic phase was dried over magnesium sulfate and the solvent was removed to give the desired product as a pale brown powder (130 mg, 53%). mp 140–142 °C; (Found: C, 38.81; H, 2.68; N, 2.70. Calc. for $C_{34}H_{28}F_{26}N_2O_6$: C, 38.72; H, 2.68; N, 2.66%); δ_H ($CDCl_3$) 6.71 (2H, d, $^3J_{HH}$ 8.6, ArH), 6.25 (2H, d, $^4J_{HH}$ 2.1, ArH), 6.16 (2H, dd, $^3J_{HH}$ 8.6, $^4J_{HH}$ 2.1, ArH), 4.05 (8H, m, $ArOCH_2$), 3.93 (8H, m, $ArOCH_2CH_2$), 3.74 (4H, t, $^3J_{HF}$ 15.9, $NHCH_2$), 2.06 (2H, br s, NH); δ_F ($CDCl_3$) −80.71 (3F, t, $^4J_{FF}$ 10.0, CF_3), −118.04 (2F, t, $^4J_{FF}$ 12.2, $NHCH_2CF_2$), −121.96 (2F, m, CF_2), −122.80 (2F, m, CF_2), −123.31 (2F, m, CF_2), −126.09 (2F, m, CF_2); δ_C ($CDCl_3$) 148.8 (C), 141.0 (C), 140.4 (C), 115.1 (CH), 103.9 (CH), 100.3 (CH), 68.9 (CH_2), 68.7 (CH_2), 67.7 (CH_2), 44.1 (t, $^2J_{CF}$ 23.6, CH_2); m/z (FAB) 1093 (MK^+, 68%), 1077 (MNa^+, 91), 1054 (M^+, 100).

4.2. *Crystal structure determination of cis-4,4′-di(1H,1H,2H,2H-perfluorodecyl)-dibenzo-18-crown-6 (**15a**)*

Single crystals were grown by slow evaporation from a solution of di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-dibenzo-18-crown-6 (**15**) in deuterated chloroform.

4.2.1. *Crystal data for (**15a**)*

$C_{40}H_{30}F_{34}O_6$, $M = 1252.64$, monoclinic, space group $P2(1)$, $a = 16.382(2)$ Å, $b = 5.1443(8)$ Å, $c = 27.152(4)$ Å, $\alpha = 90°$, $\beta = 99.122(3)°$, $\gamma = 90°$, $U = 2259.3(6)$ Å^3 (by least-squares refinement of 757 reflections), $T = 150(2)$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $Z = 2$, $D_{calc} = 1.841$ mg m^{-3}, $F(0\,0\,0) = 1248$, dimensions 0.23 mm × 0.18 mm × 0.05 mm, μ (Mo Kα) = 0.215 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.928 and 0.721, respectively, Bruker APEX 2000 CCD diffractometer, data collection range $1.52 < \theta < 25.00°$, $-19 \leq h \leq 19$, $-6 \leq k \leq 6$, $-32 \leq l \leq 32$, no crystal decay was detected; 16,538 reflections were measured and 7806 were unique ($R_{int} = 0.0600$), final $R_1 = 0.0565$, $wR_2 = 0.1015$ (0.1065 and 0.1170, respectively for all the data) for 721 variables. The final residual Fourier map showed peaks of 0.351 and −0.268 e Å^{-3}.

4.2.2. *Structure solution and refinement*

Structure solution by direct methods and structure refinement on F2 employed SHELXTL version 6.10 [39]. Hydrogen atoms were included in calculated positions (C–H = 0.95–099 Å) riding on the bonded atom with isotropic displacement parameters set to 1.2 *U*eq(C) for all H atoms. All non-H atoms were refined with anisotropic displacement parameters. The data were corrected for Lorentz and polarization effects. The crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC734950. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e mail: deposit@ccdc.cam.ac.uk).

4.3. *Sodium and potassium picrate extractions (Table 2) [7,13,38]*

Equal volumes of a dichloromethane solution (10 mL) of the required macrocycle (0.1 mM) and an aqueous solution of the sodium or potassium picrate (0.1 mM) were introduced into a stoppered flask and stirred for 30 min at 21 ± 1 °C. The mixture was allowed to stand for 2 h at the same temperature to allow complete phase separation. The absorbance of the picrate in the aqueous phase was measured at 356 nm with a Shimadzu UV–visible spectrophotometer. The percentage extraction was calculated by:

$$\%\,\text{extraction} = \left(\frac{100(\text{Abs}_{\text{before}} - \text{Abs}_{\text{after}})}{\text{Abs}_{\text{before}}}\right)$$

where $\text{Abs}_{\text{before}}$ is the absorbance of a similarly diluted sample of the unextracted potassium picrate solution and $\text{Abs}_{\text{after}}$ is the absorbance of the potassium picrate solution after extraction. Three independent extractions were performed for each combination of potassium picrate and ionophore, and the results were averaged.

4.4. *General procedure for iodide displacement under solid–liquid conditions*

A mixture of 1-bromooctane (200 mg, 1.0 mmol), potassium iodide (840 mg, 5.0 mmol), biphenyl (154 mg, 1.0 mmol), benzotrifluoride (4 mL) and the appropriate crown ether (0.02 mmol) was refluxed at 110 °C. The reaction was monitored by taking samples (25 μL) every hour for 10 h and after diluting the sample with benzotrifluoride (2 mL), it was analysed by gas chromatography to determine the conversion to product using biphenyl as the internal standard (115 °C for 3 min followed by 45 °C min^{-1} ramp to 195 °C, held for 1 min. Injector: 300 °C, detector: 300 °C. R_t 2.13 min (1-bromooctane), 2.85 min (1-iodooctane), 4.05 min (biphenyl)).

4.4.1. *General procedure for iodide displacement by supported fluorous phase catalysis (SFPC)*

Di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6 (**14**) (0.02 mmol) was supported on fluorous reverse phase silica gel (95%, w/w) by stirring in dichloromethane at 40 °C for 2 h. After cooling to room temperature, the solvent was eliminated under reduced pressure and the supported catalyst was dried under oil pump vacuum for 2 h.

A mixture of 1-bromooctane (200 mg, 1.0 mmol), potassium iodide (840 mg, 5.0 mmol), biphenyl (154 mg, 1.0 mmol), the supported perfluoroalkylated crown ether (0.02 mmol) and either THF (4 mL) or ethyl acetate (4 mL) was refluxed at 70 °C for 16 h. The reaction was monitored by taking samples (25 μL) every 2 h. After diluting the sample with the appropriate solvent (2 mL), it was analysed by gas chromatography to determine the conversion to product using biphenyl as the internal standard.

4.4.2. *General procedure for recycling (**14**) supported on fluorous reverse phase silica gel*

After 6 h the reaction mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure and the resulting solid was washed with cold hexane (25 mL, −18 °C) in order to extract the clean organic products. The insoluble supported catalyst (**14**) was filtered and washed with water (25 mL) to remove the excess potassium salts and washed again with cold hexane (20 mL, −18 °C). The supported perfluoroalkylated catalyst (**14**) was finally dried under oil pump vacuum overnight at 60 °C before being reused in the next run (Table 4).

*4.4.3. General procedure for the separation and recovery of di(1H,1H,2H,2H-perfluorooctyl)-dibenzo-18-crown-6 (**14**) after iodide displacement reaction*

After cooling to room temperature, the reaction mixture was filtered to remove the excess potassium salts which were extracted with benzotrifluoride (2 × 5 mL). The solvent was removed under reduced pressure and the resulting residue was re-dissolved in dichloromethane (5 mL). After washing with water (5 mL), the aqueous phase was extracted three times with dichloromethane (5 mL) and the combined dichloromethane extracts were dried over magnesium sulfate. After reducing the volume of solvent to 1 mL, the organic phase was passed through a short column of fluorous reverse phase silica gel (~4 g) and the column was eluted with benzotrifluoride (40 mL) to obtain the clean organic products. The fluorinated phase transfer catalyst was then recovered (92–94%) by eluting with trifluoroethanol (50 mL). The solvent was removed under reduced pressure and the phase transfer catalyst was dried *in vacuo* for 1 h at 60 °C before being reused in another aliphatic nucleophilic substitution (Table 5).

4.5. General procedure for fluoride displacement under solid–liquid conditions

A mixture of 2,4-dinitrochlorobenzene (207 mg, 1.0 mmol), biphenyl (154 mg, 1.0 mmol), spray-dried potassium fluoride (87 mg, 1.5 mmol), which had been dried previously under oil pump vacuum at 170 °C for 8 h, acetonitrile (5 mL) and the appropriate phase transfer catalyst (0.10 mmol) was refluxed at 85 °C under nitrogen. The reaction was monitored after 2 and 12 h by taking samples (25 μL), which were diluted with acetonitrile (2 mL) and analysed by gas chromatography to determine the conversion to product using biphenyl as the internal standard (115 °C for 1.2 min followed by 45 °C min^{-1} ramp to 195 °C, held for 1 min. Injector: 300 °C, detector: 300 °C. R_t 2.79 min (biphenyl), 2.92 min (2,4-dinitrofluorobenzene), 3.37 min (2,4-dinitrochlorobenzene)).

*4.5.1. General procedure for the separation and recovery of di(1H,1H,2H,2H-perfluorooctyl)-dibenzo-18-crown-6 (**14**) after fluoride displacement reaction*

After cooling to room temperature, the reaction mixture was filtered to remove the excess potassium salts which were extracted with hot dichloromethane (15 mL). The solvents were combined and eliminated under reduced pressure. The resulting residue was re-dissolved in dichloromethane (5 mL) and washed once with water (5 mL). The aqueous phase was extracted three times with dichloromethane (5 mL). The combined dichloromethane extracts were dried over magnesium sulfate. After reducing the volume of solvent to 1 mL, the organic phase was passed through a short column of fluorous reverse phase silica gel (~4 g) and the column was eluted with dichloromethane (15 mL) to obtain the clean organic products. The fluorinated phase transfer catalyst was then recovered (93–95%) by eluting with trifluoroethanol (50 mL). After removing the solvent under reduced pressure, the phase transfer catalyst was dried *in vacuo* for 2 h at 60 °C before being reused in the next run (Table 6).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.06.002.

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