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Synthesis and solid state structure of fluorous probe molecules for fluorous separation applications

H.-J. Lehmler [a,*], S. Telu [a], S.M. Vyas [a], N.S. Shaikh [a], S.E. Rankin [b], B.L. Knutson [b], S. Parkin [c]

[a] Department of Occupational and Environmental Health, University of Iowa, College of Public Health, 100 Oakdale Campus, 221 IREH, Iowa City, IA 52242-5000, USA
[b] Chemical and Materials Engineering Department, University of Kentucky, Lexington, KY 40506, USA
[c] Department of Chemistry, University of Kentucky, Lexington, KY 40536, USA

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ABSTRACT

A series of colored hydrocarbon and fluorocarbon tagged 1-fluoro-4-alkylamino-anthraquinones and 1,4-bis-alkylamino-anthraquinone probe molecules were synthesized from a (fluorinated) alkyl amine and 1,4-difluoroanthraquinone to aid in the development of fluorous separation applications. The anthraquinones displayed stacking of the anthraquinone tricycle and interdigitation of the (fluorinated) alkyl chains in the solid state. Furthermore, intramolecular N–H···O hydrogen bonds forced the hydrocarbon and fluorocarbon tags into a conformation pointing away from the anthraquinone tricycle, with the angle of the tricycle plane normal and the main (fluorinated) alkyl vector ranging from 1° to 39°. Separation of the probe molecules on fluorous silica gel showed that the degree of fluorination of the probe molecules plays only a minor role with most eluents (e.g., hexane/ethyl acetate and methyl nonafluorobutyl ethers/ethyl acetate). However, toluene as eluent caused a pronounced separation by degree of fluorination for fluorocarbon, but not hydrocarbon tagged probe molecules on both silica gel and fluorous silica gel. These studies suggest that hydrocarbon and fluorocarbon tagged anthraquinones are useful probe molecules for the development of laboratory scale fluorous separation applications.

1. Introduction

Introduction of a perfluoroalkyl group with the general structure $-C_nF_{2n+1}$ into an organic molecule conveys unique properties that are not only of interest for a broad range of industrial and consumer applications,[1] but are also used extensively in fluorous chemistry.[2–5] Applications involving fluorous synthesis and separation utilize the fact that perfluorinated compounds display weak intermolecular interactions and, therefore, are both more lipophobic and hydrophobic compared to analogous perhydrocarbon compounds. This unique combination of lipophobicity and hydrophobicity allows for the postsynthesis separation of organic (reaction) mixtures by permanently or temporarily tagging reactants and substrates with a highly fluorinated alkyl chain. After the reaction is complete, fluorous (F–)tagged molecules are separated from other mixture components by liquid–liquid extraction using a fluorous solvent or solid–liquid extraction using a fluorocarbon-functionalized solid material. This approach greatly facilitates the separation of reaction mixtures into functionally resolved fractions, which is especially advantageous in combinatorial chemistry or parallel syntheses.

Fluorocarbon-functionalized (fluorous) silica gel has been used for fluorous solid–liquid extraction,[4,6–8] the separation of fluorous compounds with varied perfluoroalkyl chain length[4,8–10] and for the immobilization of fluorous catalysts.[8,11] During fluorous solid–liquid extraction a mixture containing F-tagged as well as other organic and inorganic components is loaded onto a cartridge containing the fluorous silica gel. Components without a fluorous tag are eluted first with a fluorophobic solvent system, such as methanol/water=4:1 (v/v). Subsequently, F-tagged components are eluted with a more fluorophilic solvent system, such as methanol (see Refs. 12 and 13 for the classification of solvents based on the polarity and fluorophilicity). More complex fluorous mixtures containing components with different degrees of fluorination can be separated by fluorous chromatography on fluorous silica gel. The elution behavior of fluorous silica gel is significantly different from conventional reverse-phase C_8 or C_{18} silica gel because the fluorous tag dominates the separation over the nonfluorinated, organic part of the analytes in the presence of water in the mobile phase.

The materials used for these fluorous separation applications are primarily formed through the simple postsynthesis

* Corresponding author. Tel.: +1 319 335 4211; fax: +1 319 335 4290.
E-mail address: hans-joachim-lehmler@uiowa.edu (H.-J. Lehmler).

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attachment of the perfluoroalkyl group to porous silica particles.[2,8,14] In a typical synthesis, a fluorous chlorosilane Cl–Si(R)$_2$–(CH$_2$)$_n$R$_f$ is reacted with the surface OH groups of normal silica gel in the presence of a base to yield silica –O–Si(R)$_2$–(CH$_2$)$_n$R$_f$, where R denotes an alkyl group, such as methylene, and R$_f$ denotes a perfluoroalkyl group. Alternatively, fluorous silica gel has been prepared by postsynthesis modification of silica with (EtO)$_3$-Si(CH$_2$)$_2$C$_6$F$_{13}$ and related alkoxy silanes.[11] Several fluorocarbon-functionalized materials with R$_f$=C$_6$F$_{13}$ or C$_8$F$_{17}$ are available from commercial sources in bulk, as TLC plates or HPLC columns and have been used extensively in fluorous separations. C$_8$F$_{17}$-functionalized materials are considered to be especially advantageous for fluorous separations because of the stronger interaction of fluorinated components with the stationary phase and, thus, the requirement for less water in the eluent.[8]

We recently reported the 'one-pot' synthesis of fluorocarbon-functionalized surfactant-templated mesoporous silica as an alternative approach to materials for fluorous separation and synthesis applications.[15] In this earlier study fluorocarbon-functionalized silica was synthesized by co-condensation of tetraethoxysilane and a fluorous-tagged alkoxysilane in the presence of a hydrocarbon or fluorocarbon pore-templating agent. This direct synthesis approach has the advantage of producing materials with high functional group loading and uniform distribution compared to postsynthesis attachment of the fluorinated alkyl group.[16,17] Similar to commercial fluorous silica gel, the materials synthesized using the direct synthesis approach allowed an efficient separation of two anthraquinone probes, 1,4-bis-butylamino-anthraquinone and 1-fluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone, by solid–liquid extraction. Both anthraquinone probes have been used previously to visualize fluorous separations.[18]

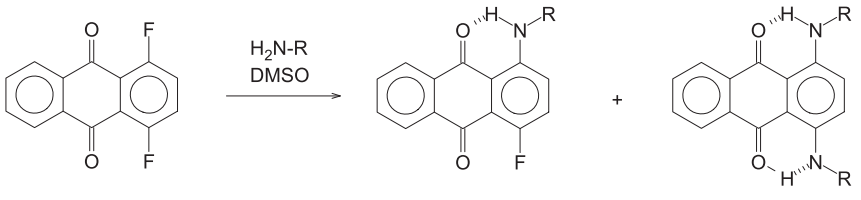
The two anthraquinone probes differ in color, and are thus ideally suited for investigations of relatively simple fluorous separations; however, they are structurally dissimilar, which makes it difficult to extrapolate to more complex fluorous separation problems involving, for example, components with different degrees of fluorination. Although several series of fluorous-tagged organic compounds, such as benzoate esters, triphenylphosphines, and *O*-benzoylmadelates, have been used to illustrate fluorous separations,[8,18,19] these compounds are not colored, which represents a drawback for their use as probe molecules, especially for fluorous separations with simple, hand-packed columns. Here, we describe the synthesis and X-ray crystallographic characterization of six hydrocarbon and eight fluorocarbon functionalized anthraquinone probes. Their separation was investigated using fluorous TLC to demonstrate that these probe molecules are suitable to investigate fluorous separations of novel fluorocarbon-functionalized materials.

2. Results and discussion

2.1. Synthesis of 1-fluoro-4-alkylamino- and 1,4-bis-alkylamino-anthraquinones

To the best of our knowledge, the synthesis and characterization of simple 1-fluoro-4-alkylamino-anthraquinones have not been reported previously. Several 1,4-bis-alkylamino-anthraquinones, such as Sudan Blue II (1,4-bis-butylamino-anthraquinone), are commercial dye products; however, the laboratory synthesis and characterization of only a few 1,4-bis-alkylamino-anthraquinones have been reported, primarily as part of studies of their solubility in supercritical carbon dioxide.[20–22] One general approach to alkylamino-anthraquinones is the nucleophilic displacement of chloride, fluoride or other leaving groups from appropriately functionalized anthraquinone precursors, an approach that has been employed for the synthesis of a variety of symmetrical and unsymmetrical 1,4-bis-alkylamino-anthraquinones.[23–25] Alternatively, symmetrical 1,4-bis-alkylamino-anthraquinones can be synthesized directly by the reaction of an alkyl amine with 1,4-dihydroxy-anthraquinone.[26]

In this study, the sequential nucleophilic displacement of fluorines from 1,4-difluoroanthraquinone **1** by appropriate alkyl and perfluoroalkylamines (**2a–c** and **5a–d**) was employed for the synthesis of 1-fluoro-4-alkylamino-anthraquinones **3a–c** and **6a–d** as well as 1,4-bis-alkylamino-anthraquinones **4a–c** and **7a–d** (Scheme 1). The



1 **3** or **6** **4** or **7**

Alkylamine (R-NH$_2$)		Reaction conditions		**3** or **6**	Yield [%]	**4** or **7**	Yield [%]
		Temperature [°C]	Time [h]				
H$_9$C$_4$-	**2a**	Ambient	24	**3a**	75	-	-
H$_{11}$C$_5$-	**2b**	Ambient	3	**3b**	63	-	-
H$_{17}$C$_8$-	**2c**	Ambient	8	**3c**	55	-	-
H$_9$C$_4$-	**2a**	110	1.5	-	-	**4a**	71
H$_{11}$C$_5$-	**2b**	110	2	-	-	**4b**	64
H$_{17}$C$_8$-	**2c**	110	2	-	-	**4c**	71
F$_7$C$_3$CH$_2$-	**5a**	110	4 d	**6a**	34	**7a**	11
F$_9$C$_4$CH$_2$-	**5b**	110	5 d	**6b**	39	**7b**	12
F$_{15}$C$_7$CH$_2$-	**5c**	110	6 d	**6c**	46	**7c**	13
F$_{17}$C$_8$CH$_2$-	**5d**	110	6 d	**6d**	43	**7d**	5

Scheme 1. Synthesis of mono- and di-substituted hydrocarbon and fluorocarbon anthraquinones.

1-fluoro-4-alkylamino-anthraquinones **3a**–**c** were isolated in 55–75% yield from the reaction of **1** with alkylamines **2a**–**c** at ambient temperature. Synthesis of 1,4-bis-alkylamino-anthraquinones **4a**–**c** required brief heating (1.5–2 h) of the reaction mixture to 110 °C. In contrast, a mixture of anthraquinones **6a**–**d** and **7a**–**d** was obtained after prolonged heating of the reaction mixture containing **1** and the symmetrical 1,4-bis-alkylamino- and 1,4-bis-arylamino-anthraquinones have been published.[28–32] Here we report the crystal structure of 1-fluoro-4-octylamino-anthraquinone **3c** and 1,4-bis-alkylamino-anthraquinones **4b** and **4c** to add to the number of available crystal structures (Figs. 1–3). We also report the structure of 1*H*,1*H*-perfluorooctylamino-anthraquinones **6c** and **7c**

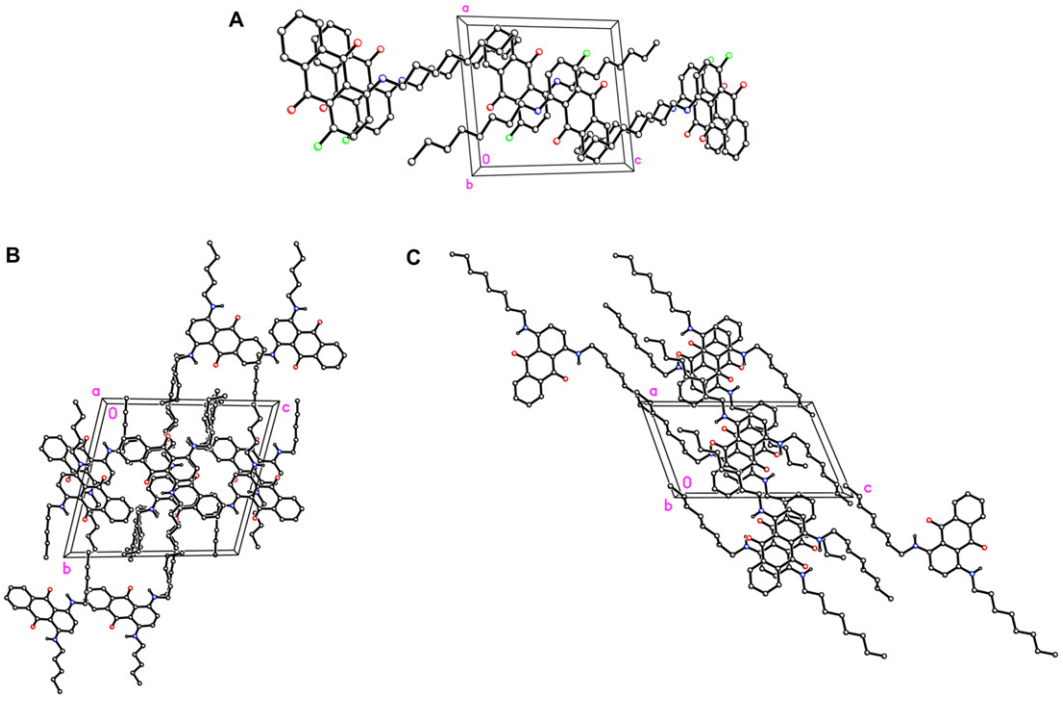


Figure 1. Packing diagrams viewed down the *b*-axis illustrating the tricycle stacking of (A) 1-fluoro-4-octylamino-anthraquinone (**3c**), (B) 1,4-bis-pentylamino-anthraquinone (**4b**) and (C) 1,4-bis-octylamino-anthraquinone (**4c**). H atoms have been omitted for clarity.

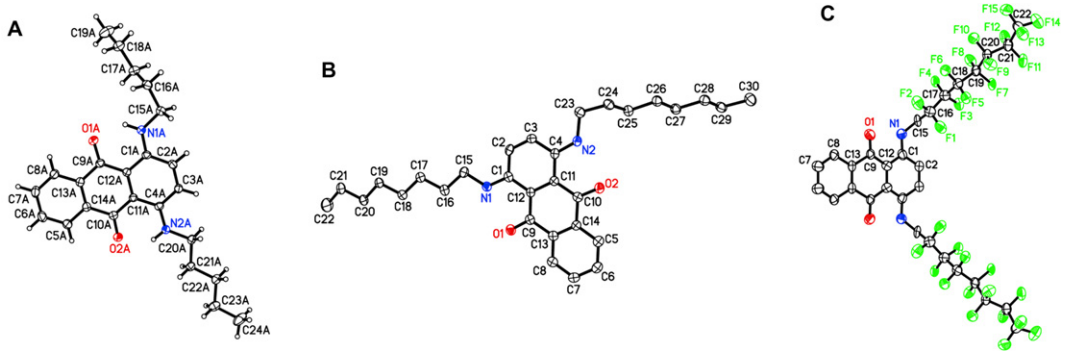


Figure 2. View of 1,4-bis-alkylamino-anthraquinones showing the atom-labeling scheme: (A) 1,4-bis-pentylamino-anthraquinone (**4b**), (B) 1,4-bis-octylamino-anthraquinone (**4c**) and (C) 1,4-bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**7c**). Displacement ellipsoids are drawn at the 50% probability level.

fluorinated alkylamines **5a**–**d** at 110 °C. The more sluggish character of the later reaction is due to the highly electronegative character of the perfluoroalkyl group of **5a**–**d**, which drastically reduces the nucleophilic character of the NH_2 group.

2.2. Solid state structure of 1-fluoro-4-alkylamino- and 1,4-bis-alkylamino-anthraquinones

Although *N*-alkyl derivatives of anthraquinones, such as Mitoxantrone, are highly effective anticancer, antimicrobial, and immunosuppressive agents,[24,27] no crystal structures of 1-fluoro-4-alkylamino-anthraquinones and only few crystal structures of (Figs. 2–4). In addition to containing the anthraquinone moiety, the structures of **6c** and **7c** are of fundamental interest because crystallographic studies of compounds containing perfluorinated chains, such as the $F_{15}C_7CH_2$-moiety, are generally difficult owing to poor crystal quality, which is a result of the weak intermolecular interactions in this type of compound and, as reviewed recently by Dey et al.,[33] the disorder of the perfluoroalkyl chains in the crystal.

Crystals of 1-fluoro-4-octylamino-anthraquinone (**3c**) were triclinic (space group *P*) with a=9.3570(3), b=9.8152(3), c=10.8332(4) Å, and α=116.3581(16)°, β=93.2401(14)°, γ=94.1698(16)°. Two molecules of **3c** formed pairs with the tricycles stacked head-to-tail (Fig. 1A). Furthermore, pairs of weak C–H···O interactions exist

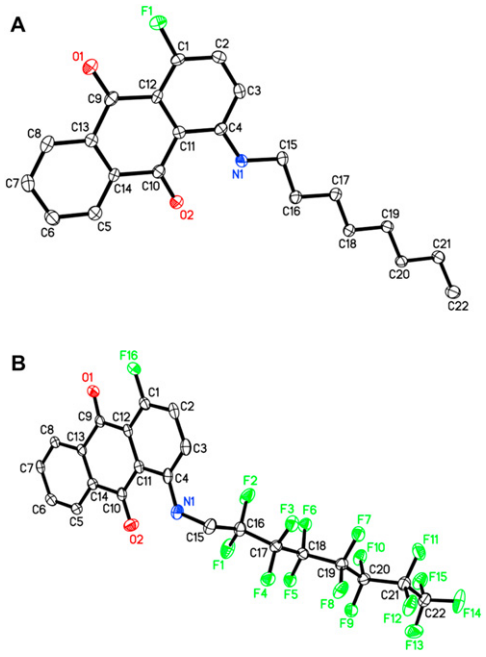


Figure 3. View of two monoalkylamino-anthraquinones showing the atom-labeling scheme: (A) 1-fluoro-4-octylamino-anthraquinone (**3c**) and (B) 1-fluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**6c**). Displacement ellipsoids are drawn at the 50% probability level.

anthraquinones **6c** and **7c** showed segregation of the electronically different parts of the anthraquinone molecules. The 1*H*,1*H*-perfluoroalkyl chains of **7c** interdigitated and the tricycles formed continuous, steeply inclined stacks, with alternate stacks creating a herringbone motif. Similar structural features can be observed for **6c**, with **6c** molecules forming bilayers.

The formation of layers of interdigitated 1*H*,1*H*-perfluoroalkyl chains by both **6c** and **7c** in particular is not surprising because A···B interactions (e.g., interactions between different parts of a molecule) are usually less favorable than the mean of A···A and B···B interactions (i.e., interactions between similar parts of a molecule).[34] This is particularly true for the hydrophobic and lipophobic perfluoroalkyl chains. Analogously, the limited number of reported crystal structures with C_7F_{15} or similar perfluoroalkyl moieties also contain interdigitated perfluoroalkyl chains.[35–40]

The solid state molecular structures of **3c**, **4b**, **4c**, **6c**, and **7c** displayed intramolecular N–H···O hydrogen bonds, which forced the adjacent alkylamino chains into a conformation pointing away from the anthraquinone tricycle (Figs. 2 and 3). The angle of 1° between the tricycle plane normal and the main (F)-alkyl vector indicates a nearly coplanar conformation for the hydrocarbon 1-fluoro-4-octylamino-anthraquinone **3c**. Similarly, at least one of the angles in **4b** and **4c** (4° and 2°, respectively) was close to a coplanar conformation. The second angle in **4b** and **4c** significantly deviated from a coplanar confirmation, with 24° and 34° for **4b** and **4c**, respectively (the angles of the second molecule of **4b** was quite similar, even though one of its chains is disordered). A pronounced

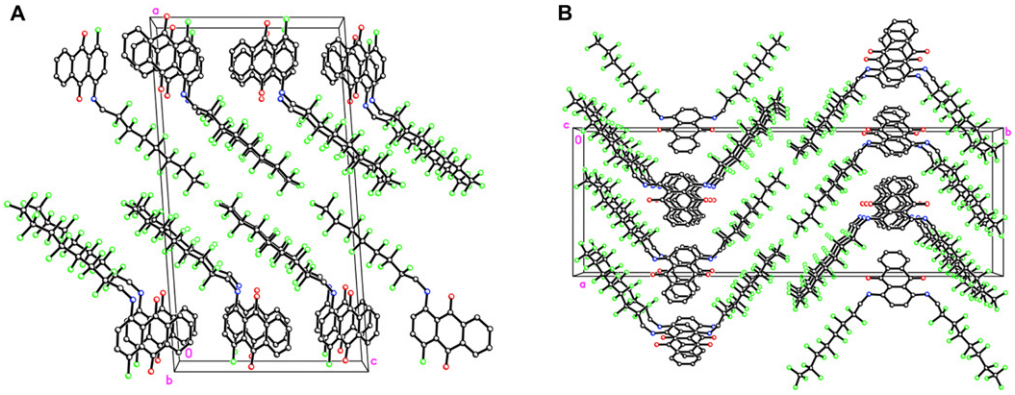


Figure 4. Packing diagrams of (A) 1-fluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**6c**) viewed down the *b*-axis and (B) 1,4-bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**7c**) viewed down the *c*-axis. Both packing diagrams illustrate the tricycle stacking and the segregation of the F–alkyl chain with some interdigitation. H atoms have been omitted for clarity.

between inversion related molecules between C8–H8···O1 (d(D–A)=3.227(3) Å, pairs related by (1−x, 1−y, 2−z)) and between C5–H5···O2 (d(D–A)=3.333(2) Å, pairs related by (−x, 1−y, 1−z)). The two hydrocarbon 1,4-bis-alkylamino-anthraquinones **4b** and **4c** were triclinic (space group $P\bar{1}$), with a=8.23800(10), b=15.6467(3), c=17.2688(3), α=101.1773(7)°, β=103.6734(6)° and γ=100.5443(7)° for **4b** and a=9.7465(2), b=10.5257(3), c=15.1675(4), α=92.9539(11)°, β=108.1349(12)° and γ=114.7648(11)° for **4c**. Compounds **3c** and **4c** displayed clear interdigitation of the alkyl chains (Fig. 1A and C); however, the pentyl chains of **4b** were not quite long enough to properly interdigitate (Fig. 1B). Similar to **3c**, the tricycles of **4b** and **4c** are stacked head-to-tail in pairs, with pairs related by inversion.

The 1-fluoro-4-perfluoroalkylamino-anthraquinone **6c** was monoclinic (space group $P2_1/c$), with a=27.190(3), b=5.2390(6), c=14.8569(16) Å, and β=93.941(3)°, and the 1,4-bis-perfluoroalkylamino-anthraquinone **7c** was orthorhombic (space group P_{nma}), with a=14.474(3), b=42.042(8), c=5.3313(11) Å. As illustrated in Figure 4, the packing diagrams of the fluorinated

deviation from the coplanar conformation of the alkyl chain was observed for **6c** and **7c**, with 39° and 37.5° (both angles of **7c**), respectively. These more or less comparable (solid state) conformations of all (fluorinated) anthraquinone probes are expected to allow for a similar interaction of the (F–)alkyl chain of the probe molecules with the F-tagged materials used in (fluorous) separations.

2.3. Separation of anthraquinones by thin layer chromatography (TLC)

The separation of the hydrocarbon and fluorocarbon 1-fluoro-4-alkylamino- and 1,4-bis-alkylamino-anthraquinones was investigated by TLC using both silica gel and fluorous silica gel as stationary phases to demonstrate the usefulness of this series of compounds for investigations of fluorous separations. Several frequently used TLC solvent systems were employed to investigate a range of solvent polarities and fluorophilicities, two factors that play an important role in fluorous separations.[12,13] Figure 5 shows a comparison of chain-length dependent changes of the R_f values of

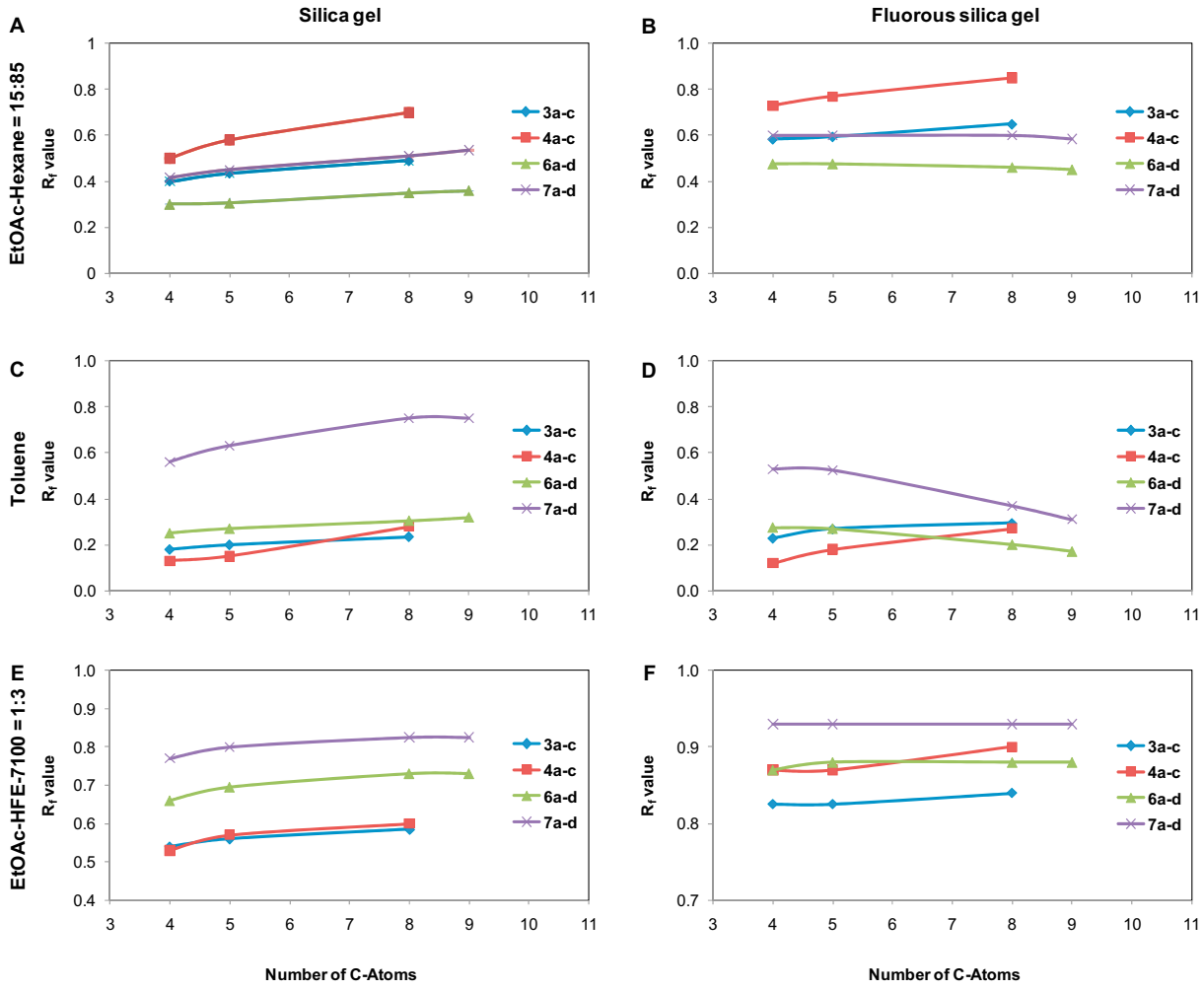


Figure 5. Comparison of chain-length dependent changes of the R_f values of the various dye molecules on silica gel and fluorous silica gel. Ethyl acetate/hexane (15:85, v/v) on (A) silica gel and (B) fluorous silica gel; toluene on (C) silica gel and (D) fluorous silica gel; ethyl acetate/HFE-7100 (1:3, v/v) on (E) silica gel and (F) fluorous silica gel (HFE-7100 is produced under the name Novec™ Engineered Fluid HFE-7100 by the 3M Company).

the various anthraquinone molecules on both stationary phases using selected mobile phases.

2.3.1. Organic solvent-based mobile phases. Several typical organic solvents, including hexane, ethyl acetate/hexane (15:85, v/v), toluene and water/methanol (1:4, v/v), were investigated as mobile phase. Hexane was initially selected as mobile phase because it is a non-polar and non-fluorophilic solvent.[12,13] All anthraquinones were retained at the baseline with hexane as eluent due to their polar character. Since the polarity of a hexane mobile phase is frequently increased by adding ethyl acetate, we subsequently investigated the separation of all anthraquinones with ethyl acetate/hexane (15:85, v/v) as mobile phase. As illustrated in Figure 5A and B, the addition of ethyl acetate indeed resulted in good separation of the various anthraquinones. The R_f values of the more polar 1-fluoro-4-alkylamino-anthraquinones **3a–c** and **6a–c** were always smaller compared to the corresponding 1,4-bis-alkylamino-anthraquinones **4a–c** and **7a–c**, independent of the stationary phase. Furthermore, the R_f values of the hydrocarbon anthraquinones were larger compared to their fluorinated counter parts (i.e., **3a–c**>**6a–c** and **4a–c**>**7a–c**) on both stationary phases. This indicates that the fluorinated anthraquinones **6a–d** and **7a–d** behave like less lipophilic compounds in this solvent system due to the high degree of fluorination.

On silica gel, an increase in the R_f values with increasing length of the alkyl chains was observed for **3a–c** and **4a–c** with the ethyl acetate/hexane mobile phase (Fig. 5A). This effect was most pronounced with the hydrocarbon 1,4-bis-alkylamino-anthraquinones **4a–c**, which are the most lipophilic compounds investigated. Similarly, the R_f values of the fluorinated anthraquinones **6a–d** and **7a–d** increased with increasing F-alkyl chain length due to the decreasing polarity of the anthraquinones. The hydrocarbon anthraquinones **3a–c** and **4a–c** also displayed an increase in R_f values with increasing chain length on fluorous silica gel. Analogous to other fluorous chromatographic separations,[4] a slight decrease in the R_f values for the fluorocarbon anthraquinones **6a–d** and **7a–d** was observed with increasing length of the F-alkyl chains, indicating the increased retention of these compounds by the fluorous silica gel with increasing degree of fluorination (Fig. 5B).

Toluene also is a comparatively non-polar solvent. However, it is considered to be more fluorophilic compared to hexane.[13] Toluene had little effect on the separation of the hydrocarbon anthraquinones **3a–c** and **4a–c** (Fig. 5C and D) on both silica gel and fluorous silica gel. The R_f values of the hydrocarbon mono- and bis-alkylamino derivatives were similar and only a slight increase in the R_f values with increasing chain length was observed on both stationary phases. Interestingly, a more dramatic effect on the separation of the fluorinated anthraquinones was observed on silica gel as well as fluorous silica gel, with the fluorinated 1,4-bis-alkylamino-anthraquinones **7a–d** being clearly separated from the corresponding fluorinated 1-fluoro-4-alkylamino-anthraquinones **6a–d**. Furthermore, the

fluorinated 1,4-bis-alkylamino-anthraquinones **7a–d** were clearly separated from the corresponding hydrocarbon analogues on silica gel (Fig. 5C), with the R_f values decreasing in the order **7a–d**>**6a–d**~**3a–c**~**4a–c**. On silica gel, the chain length dependent changes in the R_f values were comparable to those in the ethyl acetate/hexane mobile phase, with the R_f values increasing with increasing length of the (F–)alkyl chains. However, analogous to the ethyl acetate/hexane mobile phase, the R_f values of the fluorinated anthraquinones **6a–d** and **7a–d** showed a clear decrease with the increasing chain length on fluorous silica gel.

Water/methanol (1:4, v/v) was studied as a commonly used mobile phase for fluorous separations.[4,15,19] Methanol itself is a highly polar and somewhat fluorophilic solvent that is miscible with water. Because of its extreme fluorophobic character, even small quantities of water are known to dramatically increase the retention of fluorinated compounds on a fluorous stationary phase[3] or facilitate the partitioning of fluorous-tagged compounds out of a polar, water containing into a fluorophilic phase.[12,13] In our hands, only the anthraquinones with longer (F–)alkyl chains were separated on fluorous silica gel, whereas all butyl and the fluorocarbon pentyl derivatives were retained at the baseline (R_f=0).

2.3.2. Perfluorocarbon-based mobile phases. Several perfluorocarbon solvents have been used successfully in fluorous separations.[19,41–45] In comparison to conventional organic solvents, typical perfluoroalkanes are considered to be both fluorophilic and extraordinarily non-polar solvents, whereas perfluorinated ethers are classified as fluorophilic but more polar solvents.[12,13] In this study we investigated PFMC (perfluoromethylcyclohexane), FC-43 (tris(perfluorobutyl)amine), FC-75 (perfluoro-2-butyltetrahydrofuran), and HFE-7100 (mixture of methyl nonafluorobutyl ethers) as mobile phases. Similar to hexane, these four perfluorocarbon solvents alone were unsuitable mobile phases on both stationary phases, with all anthraquinone derivatives being retained at the baseline. This is not surprising because all anthraquinones, including **7c** and **7d**, are poorly soluble in these perfluorocarbon solvents. These two highly fluorinated anthraquinones are expected to be more soluble in a perfluorocarbon solvent because—based on their fluorine content of >60%[46]—they are fluorophilic. However, fluorophilicity not always predicts solubility in perfluorocarbon solvents. In fact, it is well established that increasing fluorine content can decrease the solubility in typical organic solvents.

Solvent tuning has been proposed as a general approach to overcome the limitations of pure perfluorocarbon solvents for fluorous liquid–liquid separations.[12,47] This approach can also be employed to optimize fluorous TLC separations, i.e., the polarity of a fluorophilic and non-polar perfluorocarbon mobile phase can be tuned by adding a polar organic solvent, such as ethyl acetate. In particular HFE-7100 and related hydrofluoroethers are polar, fluorophilic solvents that are suitable for this purpose because—in contrast to simple perfluoroalkanes—they are miscible with many organic solvents.[3,12] Furthermore, HFE-1000 is relatively inexpensive, environmentally safer, and comparatively non-toxic. Mobile phases containing HFE-1000 have been used for reverse fluorous solid phase extractions (i.e., the separation of fluorous-tagged products from reaction byproducts on normal silica gel).[19,47] Based on these earlier studies, we investigated ethyl acetate/HFE-7100 (1:3, v/v) as a mobile phase on both silica gel (reverse fluorous TLC) and fluorous silica gel (Fig. 5E and F) to allow a comparison with the ethyl acetate/hexane system (Fig. 5A and B).

As shown in Figure 5E, the reverse fluorous TLC approach (i.e., silica gel as stationary phase and ethyl acetate/HFE-7100 as mobile phase) resulted in the best separation of the various anthraquinones observed in this study. Specifically, the fluorinated anthraquinones **6a–d** and **7a–d** were well separated, with the more highly fluorinated anthraquinones **7a–d** having larger R_f values. Furthermore, the fluorinated anthraquinones were well separated from the corresponding hydrocarbon analogues **3a–c** and **4a–c**, with the elution order of **3a-c** and **4a-c** being reversed compared to the ethyl acetate/hexane system (Fig. 5A vs 5E). The large differences in the R_f values of the hydrocarbon and fluorocarbon anthraquinones are in agreement with an earlier study describing the efficient separation of fluorous benzoate esters from ethyl benzoate ester using reverse fluorous TLC with FC-72/Et_2O as mobile phase.[19] The R_f values of **3a–c** and **4a–c** were essentially identical, indicating that the fluorophilicity and not the lipophilicity of the analytes is critical for the separation of compounds using the HFE-7100-based solvent system.

On fluorous silica gel, all anthraquinones eluted close to the solvent front using the ethyl acetate/HFE-7100 mobile phase, with R_f values >0.8 (Fig. 5F). The overall trends in the R_f values were comparable to the TLC experiments with the ethyl acetate/hexane and toluene mobile phase (Fig. 5B and D). In short, the 1-fluoro-4-(F–)alkylamino-anthraquinones **3a–c** and **6a–c** were separated from the corresponding 1,4-bis-(F-)alkylamino-anthraquinones **4a–c** and **7a–d**, with the less polar 1,4-bis-(F-)alkylamino-anthraquinones having larger R_f values. While the R_f values of the hydrocarbon anthraquinones **3a–c** and **4a–c** increased with increasing chain length, the R_f values of the fluorinated anthraquinones **6a–d** and 7**a–d** slightly decreased. However, in contrast to the reverse fluorous TLC experiments (Fig. 5E), the fluorinated anthraquinones are not well separated from the corresponding hydrocarbon anthraquinones. In fact, the R_f values of **6a–d** and **4a–c** are essentially identical and it is unlikely that an adjustment of the mobile phase composition will result in as better separation.

3. Conclusion

To aid in investigations of novel fluorous stationary phases, we developed a straightforward synthesis of several colored hydrocarbon and fluorocarbon tagged 1-fluoro-4-alkylamino-anthraquinones (**3a–c** and **6a–d**) and 1,4-bis-alkylamino-anthraquinones (**4a–c** and **7a–d**) probe molecules from (F–)alkylamines (**2a–c** and **5a–d**) and 1,4-difluoroanthraquinone (**1**). These probe molecules adopt a (solid state) conformation that is expected to facilitate an interaction with the perfluoroalkyl chains of fluorous silica gel and other stationary phases. Because the anthraquinones are colored, straightforward TLC studies were employed to investigate their separation on silica gel and fluorous silica gel using a range of solvent systems with different polarity and fluorophilicity. In particular toluene and ethyl acetate/HFE-7100 as mobile phase allowed an efficient separation of the fluorocarbon tagged 1,4-bis-alkylamino-anthraquinones **7a–d** and 1-fluoro-4-alkylamino-anthraquinones **6a–d** from the corresponding hydrocarbon anthraquinones (**3a–c** and **4a–c**) on normal silica gel. These simple TLC experiments demonstrate that this series of colored anthraquinone probe molecules can facilitate the development of fluorous and reverse fluorous separations using novel stationary phases, such as (fluorocarbon functionalized) mesoporous silica.

4. Experimental

4.1. General

Reagent grade solvents were purchased from the Fisher Chemical Company and used as received. 1,4-Difluoroanthraquinone **1** was purchased from Sigma–Aldrich (St.Louis, MO, USA). The fluorinated alkylamines **5a–d** were obtained from SynQuest Laboratories, Inc. (Alachua, FL, USA) or Matrix Scientific LLC (Medina, NY, USA). Column chromatography was performed on silica gel (230–400 mesh size, type 60; Sorbent Technologies, Atlanta, GA, USA). Aluminum backed, silica gel coated AL SIL G/UV TLC plates (250 μm; Whatman, Germany) or FluoroFlash® TLC plates (Fluorous

Technologies Inc., Pittsburgh, PA, USA) were used for all TLC experiments. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance-300 or a Bruker DRX-400 spectrometer (Bruker; Billerica, MA, USA). Tetramethylsilane and trichlorofluoromethane were used as internal standards for recording ^{1}H and ^{19}F spectra, respectively. UV–vis spectra were recorded in spectroscopy grade methanol on a Perkin–Elmer Lambda 650 UV/VIS Spectrometer (Shelton, CT, USA). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA, USA). Melting points were determined using a Meltemp melting point apparatus (Laboratory Devices, Cambridge, MA, USA) and are uncorrected.

4.2. General experimental procedure for the preparation of 1-fluoro-4-alkylamino-anthraquinones 3a–c

Alkylamines **2a–c** (2.5 mmol) were added to a solution of 1,4-difluoroanthraquinone **1** (1 mmol) in anhydrous DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture, which turned orange in approximately 15 min, was stirred for 3–24 h at ambient temperature and monitored by TLC. Upon completion of the reaction, water (20 mL) was added and the reaction mixture was stirred for approximately 1 h. The reaction mixture was filtered; the residue was washed with water (3×50 mL) and dried under vacuum. The crude residue was purified by column chromatography on silica gel with ethyl acetate/hexane to give the respective 1-fluoro-4-alkylamino-anthraquinone dyes **3a–c**.

*4.2.1. 1-Fluoro-4-butylamino-anthraquinone (**3a**).* Thin orange needles; mp 106–108 °C (10% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 0.99 (t, J_1=7.2 Hz, 3H, $-CH_3$), 1.50 (sextet, $J\sim$7.2 Hz, 2H), 1.72 (quintet, J=7.2 Hz, 2H), 3.27 (m, 2H), 7.01 (dd, J_1=4.2 Hz, J_2=9.6 Hz, 1H), 7.27 (dd, $J\sim$9.6 Hz, 1H), 7.71 (m, 2H), 8.20 (m, 2H), 9.87 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 14.0, 20.5, 31.3, 42.9, 111.1, 120.0 (d, J=8.5 Hz), 120.1, 126.3 (d, J=25.8 Hz), 126.5, 126.7, 133.2, 133.5, 133.9, 134.4, 149.2, 153.3 (d, J=260.4 Hz), 182.5 (d, J=1.6 Hz), 184.4 (d, J=4.8 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ/ppm −125.67 (dd, J_1=4.2 Hz, J_2=11.0 Hz). Anal. Calcd for $C_{18}H_{16}FNO_2$: C, 72.71; H, 5.42; N, 4.71. Found: C, 72.97; H, 5.51; N, 4.70; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 297.32, found 297.2; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 514 (0.85×10^4), 351 (5.74×10^3).

*4.2.2. 1-Fluoro-4-pentylamino-anthraquinone (**3b**).* Thin orange needles: mp 120.5–122 °C (10% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 1.00 (t, J_1=6.9 Hz, 3H), 1.44–1.49 (m, 4H), 1.80 (quintet, J=6.9 Hz, 2H), 3.29 (m, 2H), 7.04 (dd, J_1=4.2 Hz, J_2=9.6 Hz, 1H), 7.23 (dd, $J\sim$9.6 Hz, 1H), 7.69 (m, 2H), 8.17 (m, 2H), 9.89 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 14.2, 22.6, 28.9, 29.5, 43.2, 111.1, 120.9 (d, J=8.6 Hz), 120.1, 126.2 (d, J=25.8 Hz), 126.5, 126.7, 133.1, 133.5, 133.8, 134.3, 149.1, 153.2 (d, J=260.5 Hz), 182.4 (d, J=1.6 Hz), 184.3 (d, J=4.7 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ/ppm −125.68 (dd, J_1=4.2 Hz, J_2=11.0 Hz). Anal. Calcd for $C_{19}H_{18}FNO_2$: C, 73.29; H, 5.83; N, 4.50. Found: C, 73.44; H, 5.96; N, 4.38; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 311.13, found 311.1; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 514 (1.03×10^4), 351 (6.90×10^3).

*4.2.3. 1-Fluoro-4-octylamino-anthraquinone (**3c**).* Thin orange needles; mp 109–110 °C (10% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 0.89 (m, 3H), 1.29 (m, 8H), 1.47 (m, J=6.9 Hz, 2H), 1.74 (quintet, J=7.5 Hz, 2H), 3.27 (m, 2H), 7.02 (dd, J_1=4.2 Hz, J_2=9.6 Hz, 1H), 7.28 (dd, $J\sim$9.6 Hz, 1H), 7.72 (m, 2H), 8.22 (m, 2H), 9.89 (t, J=4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 14.3, 22.9, 27.4, 29.3, 29.4, 29.5, 32.0, 43.3, 111.2, 120.1 (d, J=8.5 Hz), 120.1, 126.3 (d, J=25.8 Hz), 126.6, 126.8, 133.2, 133.6, 133.9, 134.4, 149.2, 153.3, 182.5 (d, J=1.6 Hz), 184.4 (d, J=4.8 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ/ppm −125.69 (dd, J_1=4.2 Hz, J_2=11.0 Hz). Anal. Calcd for $C_{22}H_{24}FNO_2$: C, 74.76; H, 6.84; N, 3.97. Found: C, 74.54; H, 6.91; N, 3.89; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 353.18, found 353.3; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 514 (0.87×10^4), 351 (5.96×10^3).

4.3. General experimental procedure for the preparation of 1,4-bis-alkylamino-anthraquinones 4a–c

Alkylamines **2a–c** (2.5 mmol) were added to a solution of 1,4-difluoroanthraquinone **1** (1 mmol) in anhydrous DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 1.5–2 h. The dark blue reaction mixture was subsequently allowed to cool to room temperature, water (20 mL) was added, and the mixture was stirred for 1 h. The reaction mixture was filtered, the residue washed with water (3×50 mL), and dried under vacuum. The crude residue was purified by column chromatography on silica gel with ethyl acetate/hexane.

*4.3.1. 1,4-Bis-pentylamino-anthraquinone (**4b**).* Blue flakes; mp 113–114 °C (10% ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 0.94 (t, J=7.2 Hz, 6H), 1.33–1.51 (m, 8H), 1.75 (quintet, J=7.2 Hz, 4H), 3.35 (s, 4H), 7.17 (s, 2H), 7.66–7.69 (m, 2H), 8.31–8.35 (m, 2H), 10.80 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 14.2, 22.7, 29.5, 43.2, 109.8, 123.8, 126.1, 132.1, 134.7, 146.2, 182.3. Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.99; N, 7.41. Found: C, 76.15; H, 8.11; N, 7.31; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 378.23, found 378.2; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 641 (2.42×10^4), 594 (1.92×10^4).

*4.3.2. 1,4-Bis-octylamino-anthraquinone (**4c**).* Blue flakes; mp 73–74 °C (10% ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 0.86–0.92 (m, 6H), 1.20–1.42 (m, 16H), 1.45–1.56 (m, 4H), 1.78 (quintet, J=7.2 Hz, 4H), 3.35–3.47 (br s, 4H), 7.30 (s, 2H), 7.68–7.78 (m, 2H), 8.33–8.41 (m, 2H), 10.87 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 14.3, 22.9, 27.4, 29.4, 29.6, 29.8, 32.0, 43.6, 110.4, 124.1, 126.3, 132.3, 134.6, 145.9, 182.6. Anal. Calcd for $C_{30}H_{42}N_2O_2$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.63; H, 9.19; N, 6.14; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 462.32, found 462.3; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 641 (2.42×10^4), 594 (1.93×10^4).

4.4. General experimental procedure for the preparation of the perfluorinated anthraquinones 6a–c and 7a–c

The fluorinated alkylamines **5a–d** (5.0 mmol) were added to a solution of 1,4-difluoroanthraquinone **1** (0.25 g, 1.0 mmol) in anhydrous DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture was heated to 110 °C and stirring continued for 4–6 days. The dark colored reaction mixture was allowed to cool to room temperature, water (20 mL) was added, and the mixture was stirred for 30 min. The crude product, which contained a mixture of **6a–c** and **7a–c**, was isolated as described above.

*4.4.1. 1-Fluoro-4-(2,2,3,3,4,4,4-heptafluorobutylamino)-anthraquinone (**6a**).* Reddish-orange solid; mp 151–152 °C (absolute EtOH); ^{1}H NMR (acetone-d_6, 300 MHz): δ/ppm 4.50 (dt, J_1=6.9 Hz, J_2=15.9 Hz, 2H), 7.52–7.55 (m, 2H), 7.82–7.90 (m, 2H), 8.13–8.17 (m, 1H), 8.22–8.26 (m, 1H), 10.19 (t, J=5.5 Hz, 1H); ^{13}C NMR (acetone-d_6, 100 MHz): δ/ppm 43.2 (t, J=23.8 Hz), 114.2, 122.2, 122.5 (d, J=9.0 Hz), 127.0 (d, J=25.4 Hz), 127.2, 127.5, 134.5, 134.8, 134.8, 135.0, 149.2, 154.8 (d, J=258.6 Hz), 182.0 (d, J=1.7 Hz), 186.1 (d, J=4.3 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.55 (t, J=9.6 Hz, CF_3), −117.58 (CF_2), −123.42 (m, Ar–F), −126.94 (t, J=2.5 Hz, CF_2). Anal. Calcd for $C_{18}H_9F_8NO_2$: C, 51.08; H, 2.14; N, 3.31. Found: C, 50.92; H, 2.14; N, 3.25; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 423.05, found 423.0; ($M^{+\bullet}-C_3F_7$), calcd 254.06, found

254.1; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 475 (1.03×10^4), 305 (5.26×10^3).

*4.4.2. 1-Fluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentylamino)-anthraquinone (**6b**).* Reddish-orange solid; mp 111–112 °C (absolute EtOH); ^{1}H NMR (acetone-d_6, 300 MHz): δ/ppm 4.52 (dt, J_1=6.9 Hz, J_2=15.9 Hz, 2H), 7.50–7.58 (m, 2H), 7.83–7.91 (m, 2H), 8.14–8.17 (m, 1H), 8.24–8.27 (m, 1H), 10.21 (t, J=5.7 Hz, 1H); ^{13}C NMR (acetone-d_6, 75 MHz): δ/ppm 43.1 (t, J=23.1 Hz), 114.2, 122.2, 122.5 (d, J=9.0 Hz), 128.0 (d, J=25.0 Hz), 128.2, 128.5, 134.5, 134.8, 134.8, 134.9, 149.2, 154.8 (d, J=260.1 Hz), 182.0 (d, J=1.9 Hz), 186.0 (d, J=4.4 Hz); ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.80 (m, CF_3), −116.92 (m, CF_2), −123.4 to −123.6 (m, Ar−F and CF_2), −125.68 (m, CF_2). Anal. Calcd for $C_{19}H_9F_{10}NO_2$: C, 48.22; H, 1.92; N, 2.96. Found: C, 48.16; H, 1.82; N, 2.98; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 473.07, found 473.2; ($M^{+\bullet}-C_4F_9$), calcd 254.06, found 253.9; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 475 (1.04×10^4), 305 (5.31×10^3).

*4.4.3. 1-Fluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**6c**).* Orange solid; mp 127–128 °C (10% ethyl acetate/hexane); ^{1}H NMR (acetone-d_6, 300 MHz): δ/ppm 4.54 (dt, J_1=6.9 Hz, J_2=15.9 Hz, 2H), 7.55–7.59 (m, 2H), 7.86–7.91 (m, 2H), 8.13–8.17 (m, 1H), 8.22–8.27 (m, 1H), 10.24 (t, J=6.5 Hz, 1H); ^{19}F NMR (acetone-d_6, 300 MHz): δ/ppm −80.55 (t, J=10.0 Hz, CF_3), −116.72 (m, CF_2), −121.33 (m, 2×CF_2), −122.22 (m, CF_2), −122.50 (m, CF_2), 123.38 (dd, J_1=5.4 Hz, J_2=9.8 Hz, Ar−F), −125.68 (m, CF_2). Anal. Calcd for $C_{22}H_9F_{16}NO_2$: C, 42.39; H, 1.46; N, 2.25. Found, C, 42.32; H, 1.31; N, 2.22; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 623.05, found 623.0; ($M^{+\bullet}-C_3F_7$), calcd 254.06, found 254.4; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 475 (1.23×10^4), 305 (6.63×10^3).

*4.4.4. 1-Fluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl amino)-anthraquinone (**6d**).* Orange needles; mp 127–128 °C (ethyl acetate); ^{1}H NMR (acetone-d_6, 400 MHz, 40 °C): δ/ppm=4.54 (dt, J_1=6.8 Hz, J_2=15.7 Hz, 2H), 7.52–7.61 (m, 2H), 7.82–7.92 (m, 2H), 8.15–8.21 (m, 1H), 8.24–8.32 (m, 1H), 10.22 (t, J=6.0 Hz, 1H); ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.48 (t, J=10.0 Hz, CF_3), −116.66 (s, CF_2), −121.24 (s, 3×CF_2), −122.12 (m, CF_2), −122.41 (m, CF_2), −123.37 (dd, J_1=5.3 Hz, J_2=9.8 Hz, Ar−F) −125.60 (m, CF_2). Anal. Calcd for $C_{23}H_9F_{18}NO_2$: C, 41.03; H, 1.35; N, 2.08. Found: C, 41.17; H, 1.27; N, 2.06; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 673.07, found 673.1; ($M^{+\bullet}-C_8F_{17}$), calcd 254.06, found 253.5; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 475 (1.17×10^4), 305 (5.39×10^3).

*4.4.5. 1,4-Bis(2,2,3,3,4,4,4-heptafluorobutylamino)-anthraquinone (**7a**).* Blue solid; mp 142–143 °C (absolute EtOH); ^{1}H NMR (acetone-d_6, 400 MHz): δ/ppm 4.52 (dt, J_1=5.1 Hz, J_2=12.0 Hz, 4H), 7.65 (s, 2H), 7.82–7.86 (m, 2H), 8.29–8.33 (m, 2H), 10.77 (t, J=4.5 Hz, 2H); ^{13}C NMR (acetone-d_6, 400 MHz): δ/ppm 42.9 (t, J=16.8 Hz), 112.6, 124.3, 127.2, 134.1, 135.1, 146.3, 184.8; ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.55 (t, J=9.5 Hz, CF_3), −117.59 (sextet, CF_2), −126.93 (t, J=2.5 Hz CF_2). Anal. Calcd for $C_{22}H_{12}F_{14}N_2O_2$: C, 43.87; H, 2.01; N, 4.65. Found: C, 43.70; H, 1.98; N, 4.56; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 602.07, found 602.1; ($M^{+\bullet}-C_3F_7$), calcd 433.08, found 433.1; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 599 (1.31×10^4), 561 (1.4×10^4).

*4.4.6. 1,4-Bis(2,2,3,3,4,4,5,5,5,5-nonafluoropentylamino)-anthraquinone (**7b**).* Blue solid; mp 118–120 °C (absolute EtOH); ^{1}H NMR (acetone-d_6, 300 MHz): δ/ppm 4.50 (dt, J_1=6.9 Hz, J_2=15.9 Hz, 4H), 7.60 (s, 2H), 7.78–7.82 (m, 2H), 8.25–8.29 (m, 2H), 10.74 (t, J=6.6 Hz, 2H); ^{13}C NMR (acetone-d_6, 75 MHz): δ/ppm 43.1 (t, J=22.6 Hz), 112.6, 124.2, 127.2, 134.0, 135.0, 146.3, 184.8; ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.80 (m, CF_3), −116.95 (m, CF_2), −123.50 (m, CF_2), −125.68 (m, CF_2). Anal. Calcd for $C_{24}H_{12}F_{18}N_2O_2$: C, 41.04; H, 1.72; N, 3.99. Found: C, 41.30; H, 1.91; N, 3.89; mass spectrum (solid probe; m/z): $M^{+\bullet}$, calcd 702.06, found 702.3; ($M^{+\bullet}-C_4F_9$), calcd 483.07, found 483.2; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 599 (1.19×10^4), 561 (1.27×10^4).

*4.4.7. 1,4-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctylamino)-anthraquinone (**7c**).* Thin, dark blue flakes; mp 157–158 °C (ethyl acetate); ^{1}H NMR (acetone-d_6, 400 MHz, 40 °C): δ/ppm 4.52(dt, J_1=6.8 Hz, J_2=14.8 Hz, 4H), 7.67(s, 2H), 7.82–7.87 (m, 2H), 8.31–8.34 (m, 2H), 10.81 (t, J=7.4 Hz, 2H); ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.29 (t, J=9.8 Hz, CF_3), −116.50 (m, CF_2), −121.04 (m, CF_2), −121.24 (m, CF_2), −121.94 (m, CF_2), −122.23 (m, CF_2), −125.43 (m, CF_2). Anal. Calcd for $C_{30}H_{12}F_{30}N_2O_2$: C, 35.95; H, 1.21; N, 2.80. Found: C, 35.92; H, 1.23; N, 2.77; mass spectrum (solid probe; m/z): ($M^{+\bullet}-C_7F_{15}$), calcd 633.07, found 633.0; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 599 (1.00×10^4), 561 (1.07×10^4).

*4.4.8. 1,4-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononylamino)-anthraquinone (**7d**).* Blue solid; mp 142–143 °C (ethyl acetate); ^{1}H NMR (acetone-d_6, 400 MHz, 40 °C): δ/ppm 4.53 (m, 4H), 7.67 (s, 2H), 7.80–7.90 (m, 2H), 8.30–8.40 (m, 2H), 10.77 (m, 2H); ^{19}F NMR (acetone-d_6, 282 MHz): δ/ppm −80.29 (t, J=9.7 Hz, CF_3), −116.78 (m, CF_2), −121.33 (m, 3×CF_2), −122.22 (m, CF_2), −122.49 (m, CF_2), −125.70 (m, CF_2). Anal. Calcd for $C_{32}H_{12}F_{34}N_2O_2$: C, 34.84; H, 1.10; N, 2.54. Found: C, 34.72; H, 1.03; N, 2.55; mass spectrum (solid probe; m/z): ($M^{+\bullet}-C_8F_{17}$), calcd 683.06, found 683.2; UV–vis (methanol): λ/nm (ε/m^{-1} cm^{-1}) 599 (1.19×10^4), 561 (1.27×10^4).

4.5. X-ray crystal structure analysis

X-ray diffraction data were collected at 90.0(2) K on either a Nonius KappaCCD or a Bruker-Nonius X8 Proteum diffractometer with graded-multilayer focusing optics as described previously.[48,49] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 762437–762441. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.02.018.

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