

Late-Stage Photocatalytic Fluoroalkylation of Aromatic Crown Ethers in Aqueous Media

Damian E. Yerien,^{+, [a, b]} Jessica Groppi,^{+, [a]} Al Postigo,^[b] Alberto Credi,^[a, c] Romina S. Conde,^[b] Massimo Baroncini,^{*, [a, d]} and Sebastian Barata-Vallejo^{*, [a, b]}

Modified crown ethers are fundamental building blocks in supramolecular chemistry, with applications in phase transfer catalysis, metal extraction, smart materials, and molecular machines. Here we report on a one-pot highly chemo- and regioselective photocatalytic fluoroalkylation protocol for the mono-functionalization of benzo substituted crown ethers. For this important class of macrocycles, the method described here

represents one of the few late-stage functionalization procedures that is both high yielding and scalable. Because of its breadth of scope and substrate tolerance, the devised approach can be applied to a wide range of aromatic crown ethers (18 examples, up to 99% yield), including those engaged in mechanically interlocked molecules.

Introduction

Fluoroalkylation has become a mainstay for the development of tailored molecular architectures in a variety of research areas, ranging from medicinal chemistry to agrochemistry,^[1–4] from materials science to nanotechnology.^[5,6] This is due to the unique characteristics imparted to organic compounds by fluorine atoms appended to their skeleton.^[7] Above all, radical fluoroalkylation reactions initiated by light-mediated catalytic systems have become considerably popular during the last ten years and are now mainstream among radical initiating methodologies.^[8] This is primarily because visible-light photo-

redox catalysis offers a versatile, green, and efficient way to introduce fluorinated moieties for a broad variety of synthetic targets.^[9,10]

Although crown ethers represent particularly interesting targets for this class of functionalization reactions, they have received little attention so far.^[11] Indeed, viable synthetic routes to substituted crown ethers are essential to exploit in full the unique properties of these macrocycles for diverse applications in science and technology.^[12] Functionalized crown ethers are accessible by templated macrocyclization using appropriately substituted starting materials,^[13] however, these are usually long, tedious, and low yielding procedures, hence direct functionalization methodologies are highly desired. Despite this, there are few reports on the direct perfluoroalkylation of (benzo)crown ethers; in addition, existing protocols involve uncommon reagents under harsh reaction conditions that result in multiple perfluoroalkyl group substitutions, making them impractical due to poor yields and time-consuming purification steps.^[14–17]

The lack of effective post-synthetic modification protocols applicable to crown ether macrocycles is particularly limiting considering that crown ethers are one of the most important and useful class of macrocyclic hosts in inorganic and supramolecular chemistry, owing to their ability to complex a wide range of inorganic and organic cations as well as neutral and even anionic guest species.^[11,18] Indeed, the utilization of crown ethers in several areas of fundamental and applied chemistry strongly relies on their functionalization in order to obtain host compounds with tailor-made properties able to be incorporated into sophisticated architectures.^[11,19,20]

Fluoroalkylated crown ethers are known to display chemical-physical characteristics that impact on their host-guest features/interactions, which are markedly different from their non-fluoroalkylated analogs as a consequence of the negative inductive effect of fluorinated chains.^[16] Indeed, fluorine functionalized crown ethers have already been extensively applied in fluorous phases for transporting/sequestering metallic ions, and as phase transfer catalysts.^[15,21] Surely, if readily

[a] Dr. D. E. Yerien,⁺ Dr. J. Groppi,⁺ Prof. A. Credi, Prof. M. Baroncini, Dr. S. Barata-Vallejo
CLAN-Center for Light Activated Nanostructures - Istituto ISOF-CNR
via Gobetti 101
40129 Bologna (Italy)
E-mail: sebastian.barata@isof.cnr.it

[b] Dr. D. E. Yerien,⁺ Prof. A. Postigo, R. S. Conde, Dr. S. Barata-Vallejo
Universidad de Buenos Aires – Facultad de Farmacia y Bioquímica
Departamento de Ciencias Químicas
Junin 954, 1113 Buenos Aires (Argentina)

[c] Prof. A. Credi
Dipartimento di Chimica Industriale
"Toso Montanari", Università di Bologna
viale del Risorgimento 4
40136 Bologna (Italy)

[d] Prof. M. Baroncini
Dipartimento di Scienze
e Tecnologie Agro-alimentari
Università di Bologna
viale Fanin 44, 40127 Bologna (Italy)
E-mail: massimo.baroncini@unibo.it

[†] These authors contributed equally to this work.

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available, they would be a significant contribution to the toolkit of molecular machinists and supramolecular chemists in general.^[22]

Here we report on a highly chemo- and regioselective protocol for the one-pot late-stage fluoroalkylation of aromatic crown ethers in aqueous media. The presented synthetic protocol allows for the introduction of fluoroalkyl chains of different lengths in high yields and with the use of readily available perfluoroalkyl group precursors and catalysts to a vast array of benzo-substituted crown ethers. The developed fluoroalkylation methodology can work reliably and selectively also on crown ethers engaged in a mechanical bond in rotaxane-type architectures, thereby opening the way to the efficient post-synthetic diversification of mechanically interlocked architectures (MIMs). Furthermore, the strong chemo-selectivity toward monosubstitution and precise regioselectivity in the perfluoroalkyl substituent grafting, as well as the option to include stereodirecting auxiliaries, raise the possibility of expanding the technique for the rapid and direct synthesis of nontrivial stereoisomeric MIMs.

Results and Discussion

Given the electron rich nature of benzo crown ethers, we decided to explore their reactivity towards electrophilic fluoroalkyl R_F radicals. We were inspired by the photocatalytic fluoroalkylation reactions mediated by organic dyes such as Rose Bengal, Eosin Y, Red Nile, and Methylene Blue. These organic dyes are good alternatives to metal complexes due to their high molar absorption coefficients, low cost, nontoxicity,

and ease of separation from reaction mixtures.^[8,9] In order to identify the best reaction conditions, we performed a series of optimization studies employing dibenzo[18]crown-6 (DB18 C6) **1** as the model substrate and perfluorohexyl iodide $n\text{-C}_6\text{F}_{13}\text{-I}$ as a $n\text{-C}_6\text{F}_{13}^{\bullet}$ radical precursor (Table 1). We commenced our investigations employing Rose Bengal (RB) as photocatalyst, N,N,N',N' -tetramethylethylenediamine (TMEDA) as additive/electron donor in MeCN as solvent.^[23] Irradiation of an argon-purged MeCN solution of **1**, RB, TMEDA and $n\text{-C}_6\text{F}_{13}\text{-I}$ with high power LEDs ($\lambda = 525$ nm, 3 W) afforded a 20% yield of product **2** (entry 1, Table 1) and 80% of the unreacted substrate **1**. In an attempt to improve the reaction yield, RB photocatalyst was replaced by Eosin Y (EY)^[24] affording **2** in 25% yield (entry 2, Table 1) along with 75% of unreacted substrate **1**. Moreover, when replacing MeCN as solvent with an MeCN : H₂O (9:1) mixture, product **2** yield increased to 45% and 48% when RB and EY were used respectively as photocatalysts (entries 3 and 4, Table 1). Intrigued by the increase observed in product **2** yield when water is introduced as co-solvent in the photocatalytic system, MeCN : H₂O (1:1) mixtures were investigated as the reaction medium. Unfortunately, substrate **1** was not soluble in such mixed solvent and precipitated as a white solid upon water addition. To overcome this drawback, KCl was added to the reaction medium – taking advantage of the strong binding capacity of crown ethers with metal cations^[18] – in order to form the $[1\text{-K}]^+$ complex which resulted thoroughly soluble in the MeCN : H₂O (1:1) (see Figure S2 in ESI). Gratifyingly, when the reaction was performed in MeCN : H₂O (1:1) with the addition of KCl, product **2** yield increased to 61% using RB as photocatalyst (entry 5, Table 1) and significantly boosted to 90% when RB was replaced with EY (entry 6, Table 1), while

Table 1. Optimization of reaction conditions. Use of dibenzo-18-crown-6 **1** (0.2 mmol) as substrate and n -perfluorohexyl iodide as fluoroalkylating reagent.

Entry	Catalyst	Additive	M^+X^-	Solvent	Product Yield [%]
1	RB	TMEDA	–	MeCN	20
2	EY	TMEDA	–	MeCN	25
3	RB	TMEDA	–	MeCN : H ₂ O (9:1)	45
4	EY	TMEDA	–	MeCN : H ₂ O (9:1)	48
5	RB	TMEDA	KCl	MeCN : H ₂ O (1:1)	61
6	EY	TMEDA	KCl	MeCN : H ₂ O (1:1)	90
7	EY	TEOA	KCl	MeCN : H ₂ O (1:1)	60
8	EY	TEA	KCl	MeCN : H ₂ O (1:1)	25
9	EY	Cs ₂ CO ₃	KCl	MeCN : H ₂ O (1:1)	50
10	EY	TMEDA	KCl	MeCN : H ₂ O (1:1)	90 ^[a]
11	EY	TMEDA	KPF ₆	MeCN	10
12	EY	TMEDA	–	MeCN : H ₂ O (1:1)	40
13	EY	TMEDA	TBACl	MeCN : H ₂ O (1:1)	40
14	EY	TMEDA	KCl	MeCN : H ₂ O (1:1)	21 ^[b]
15	EY	TMEDA	KCl	MeCN : H ₂ O (1:1)	52 ^[c]
16	EY	TMEDA	KCl	MeCN : H ₂ O (1:1)	70 ^[d,e]

[a] Without Ar-purging; [b] with 1 equiv. of $n\text{-C}_6\text{F}_{13}\text{-I}$; [c] with 2 equiv. of $n\text{-C}_6\text{F}_{13}\text{-I}$; [d] with 4 equiv. of $n\text{-C}_6\text{F}_{13}\text{-I}$; [e] di-substituted products detected by ¹H and ¹⁹F NMR.

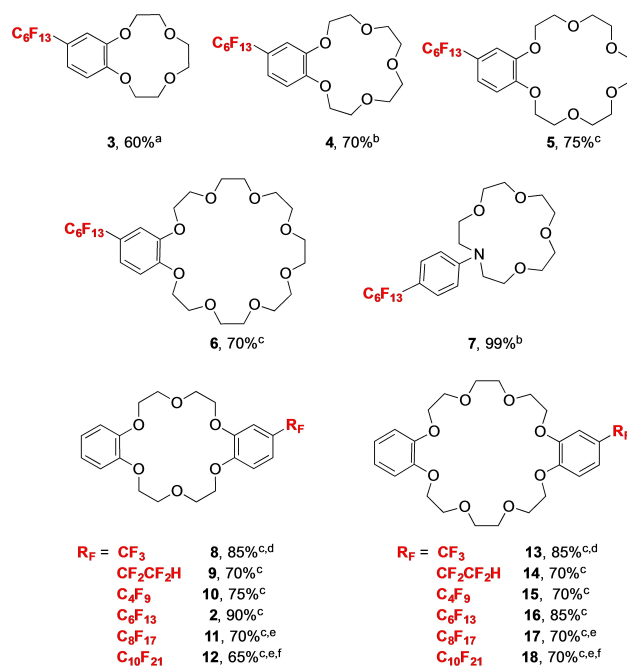
preserving an outstanding chemo and regioselectivity in the products formed.

After establishing EY as the optimum photocatalyst for the reaction, other additives/electron donors alternatives such as triethanolamine (TEOA), triethylamine (TEA) and Cs_2CO_3 were tested, affording product **2** yields of 60%, 25% and 50%, respectively (entries 7, 8 and 9, Table 1). Clearly, TMEDA (entry 6, Table 1) performed better than the alternatives studied. With the intention of simplifying the experimental set-up, the reaction was performed without Ar-purging and in the presence of air, successfully affording product **2** (entry 10, Table 1) in a comparable yield to the Ar-purged conditions (entry 6, Table 1).

However, when the EY-photocatalyzed reaction was carried out in sole MeCN as solvent, adding KPF_6 (a K^+ salt thoroughly soluble in MeCN) to form a MeCN-soluble $[\text{1}\cdot\text{K}]^+$ complex (see ESI for details), only a 10% yield of product **2** (entry 11, Table 1) was afforded. This result is very interesting, suggesting that the presence of water in the reaction media is crucial for maximizing the reaction product yield.

On the other hand, if the EY-photocatalyzed reaction is performed in MeCN : H_2O (1:1) mixture and without the addition of KCl, even though substrate **1** remains visibly insoluble, a 40% yield of product **2** (entry 12, Table 1) is still obtained. Upon replacing KCl with tetrabutylammonium chloride (TBACl) – an organic salt bearing a cation incapable of complexing with **1** due to the small cavity^[25] – and employing MeCN : H_2O (1:1) as the solvent mixture, the reaction also yielded 40% of product **2** (entry 13, Table 1). This latter result confirms that complexation of the crown cavity is necessary for maximizing the reaction yield under optimized reaction conditions (entry 10, Table 1). In an attempt of improving the overall atom economy of the reaction we determined that reducing the quantity of $n\text{-C}_6\text{F}_{13}\text{-I}$ below 3 equiv. considerably lowers product yield (entries 14 and 15, Table 1), most likely as a result of a slower radical reaction. On the other hand, increasing the amount of $n\text{-C}_6\text{F}_{13}\text{-I}$ above 3 equiv., lead to the formation of undesired mixtures of mono- and di-substituted products (entry 16, Table 1). As for the regiochemistry of the reaction, the mono-substitution takes place solely at the position shown in product **2**, which is in agreement with the reactivity of 1,2-dialkoxy arenes towards perfluoroalkyl radicals reported in our previous publication.^[26]

With the optimized conditions in hand (entry 10, Table 1), we performed the direct visible light-photocatalyzed fluoroalkylation of a series of aromatic crown ethers with different polyether ring sizes as reported in Scheme 1. To achieve the complexation necessary for maximizing the reaction yield and ensure the uptake of the substrate into the aqueous solution, the alkali metal cation (M^+) was carefully chosen for each substrate according to the polyether ring size.^[18] Interestingly, although these crown ethers necessitate an M^+ species to afford good yields of photocatalyzed R_F -substitution, in all cases the products were isolated and characterized as the neutral molecules and not as M^+ complex products (see ESI for details).



^a LiCl used; ^b NaCl used; ^c KCl used; ^d with 2 equiv of CF_3I ; ^e with 1.5 equiv of TBACl; ^f MeCN:H₂O (9:1) as solvent

Scheme 1. Scope evaluation of late-stage photocatalyzed fluoroalkylation of aromatic crown ethers. Standard conditions: Aromatic crown ether (0.2 mmol), perfluoroalkyl iodide (3 equiv), Eosin Y (EY, 5 mol%), tetramethylethylenediamine (TMEDA, 3 equiv), alkali chloride (1.2 equiv), in MeCN : H_2O (1 : 1, 3 mL), 3 W green LED, 20 hrs., r.t.

When benzo[12]crown-4 (B12 C4) was allowed to react under the optimized reaction conditions and upon the addition of LiCl, 60% yield of mono-perfluorohexylated derivative **3** was obtained as the sole product. The reaction proved also successful for benzo[15]crown-5 (B15 C5) which upon addition of NaCl afforded solely the mono-perfluorohexylated derivative **4** in 70% yield (Scheme 1). For benzo[18]crown-6 (B18 C6) and benzo[24]crown-8 (B24 C8), KCl was used for optimal complexation; both substrates gave 75% and 70% yields of the corresponding mono-perfluorohexylated derivatives **5** and **6**, respectively (Scheme 1).

Under the standard reaction conditions and upon addition of NaCl, *N*-phenylaza[15]crown-5 (Ph-N15C5) afforded 99% yield of the mono-perfluorohexylated Ph-N15C5 **7** (Scheme 1). This higher yielding reaction is in agreement with results previously reported by some of us, where fluoroalkyl radicals proved to be more reactive towards aminoaromatic compounds when compared to 1,2-dialkoxy arenes.^[26]

Encouraged by the above results, the scope of the reaction was further expanded to other fluoroalkyl radical precursors. For doing so, we focused our efforts employing DB18 C6 and dibenzo[24]crown-8 (DB24 C8) as substrates; being DB18 C6 a frequently studied crown ether in the field of phase transfer catalysis and ion transfer across membranes, and DB24 C8 commonly used as precursor to mechanically interlocked molecules (MIMs). A variety of fluoroalkyl iodides, such as trifluoromethyl, 1,1,2,2-tetrafluoroethyl, *n*-perfluorobutyl, *n*-per-

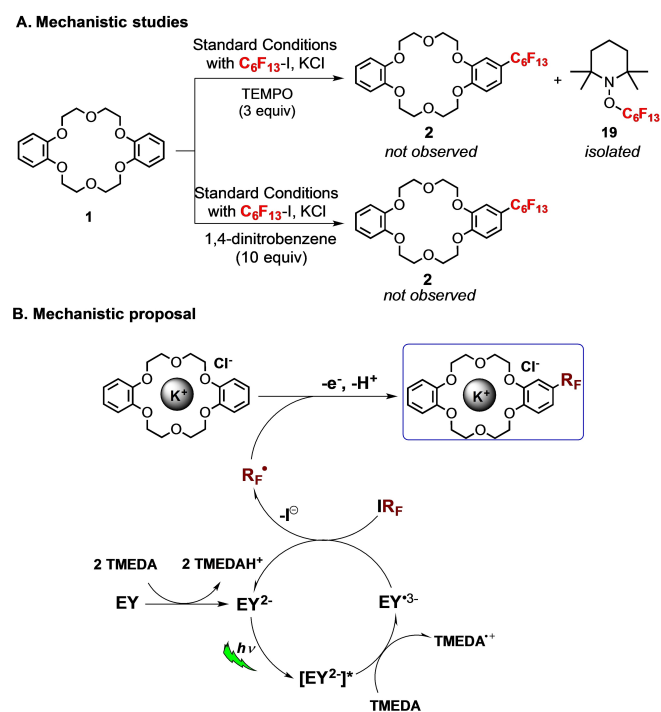
fluorooctyl and *n*-perfluorodecyl, were found to be suitable perfluoroalkyl radical precursors for affording the expected perfluoroalkylated products **8–12** in 65 to 90% yields when DB18 C6 was employed as substrate and under the optimized reaction conditions (Scheme 1).

The reaction also performed well with DB24 C8, a crown ether with a larger cavity, affording the corresponding perfluoroalkylated products **13–18** in 70 to 85% yields (Scheme 1). This is a substantial increase in yield with respect to a previous exploratory result.^[26] When *n*-C₈F₁₇I and *n*-C₁₀F₂₁I were used as fluoroalkyl radical sources, tetrabutylammonium chloride was added as phase transfer catalyst in order to maximize the reaction yields.

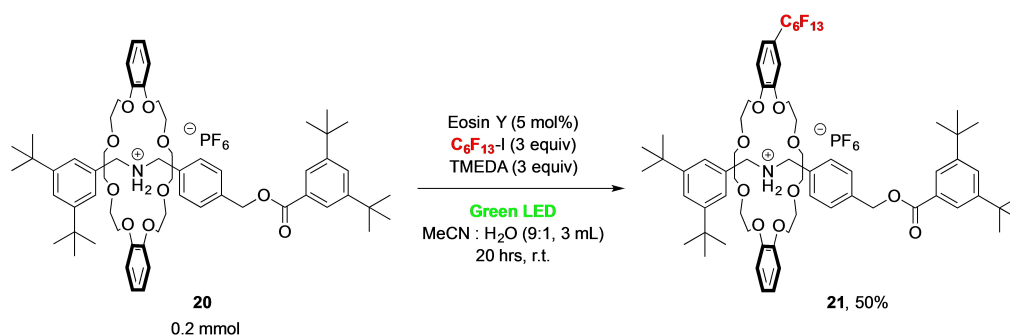
Although a mechanistic proposal for EY-photocatalyzed perfluoroalkyl radical generation has been reported in MeCN as the solvent and TMEDA as electron donor,^[27] some mechanistic aspects of the current reaction in aqueous phase have been studied. Under standard conditions and employing **1** as substrate in the presence of TEMPO, product **2** formation was completely suppressed and a TEMPO-C₆F₁₃ adduct **19** was isolated from the reaction medium (Scheme 2A), supporting the operation of a radical pathway involving C₆F₁₃• radicals. Additionally, when 1,4-dinitrobenzene is added to the reaction and employing **1** as substrate, no product **2** formation is found (Scheme 2A), confirming the presence of an electron transfer process involving reducing species. According to the investigations performed and the information available in the literature,^[27–32] a plausible reaction mechanism is proposed in Scheme 2B. Under the reaction conditions studied, EY which contains two relatively acidic protons (pK_a 2.0, 3.8 in water)^[28] is easily deprotonated by TMEDA, resulting in the quantitative

generation of EY²⁻. As opposed to EY, EY²⁻ exhibits a strong absorption in the green region of the UV-vis spectra.^[28] In the context of photoredox catalysis and upon green light illumination, the triplet state is typically considered to be the most relevant excited state for EY²⁻ due to its very brief singlet life time.^[29] Additionally, the ³[EY²⁻]* state can act both as a moderate oxidant and reductant. We presume that under the reaction conditions studied EY²⁻ acts as an oxidant accepting and electron from TMEDA; this is supported by a ΔG_{PET} for this process of -0.36 eV (E_{red}(³[EY²⁻]* / EY^{3-•}) = 0.83 V vs. SCE in MeCN:H₂O (1:1); E_{ox}(TMEDA^{•+} / TMEDA) = 0.47 V vs. SCE),^[29,30] which suggests a quite favourable spontaneous electron transfer. On the other hand, an oxidative quenching process (where ³[EY²⁻]* reduces *n*-C₆F₁₃I to C₆F₁₃• radicals and I⁻, and ³[EY²⁻]* is oxidized to [EY^{-•}]) would be a thermodynamically unfavourable event having a ΔG_{PET} of +0.27 eV for the reaction with C₆F₁₃I (E_{red}(C₆F₁₃I / C₆F₁₃I^{•-}) = -1.38 V vs. SCE in MeCN; E_{ox}(EY^{-•} / ³[EY²⁻]*) = -1.11 V vs. SCE in MeCN:H₂O (1:1)).^[29,31] The participation of EY^{3-•} in the mechanism could also be singled out by the lack of product accumulation when the reaction is done under the presence of 1,4-dinitrobenzene (*vide supra*). Then, perfluoroalkyl radicals (R_F•) could be generated by reaction of EY^{3-•} from the corresponding perfluoroalkyl iodides (R_FI). The R_F• radical formed, reacts with the (di)benzo crown ether metal cation complex via a homolytic aromatic substitution mechanism^[32] affording the perfluoroalkylated reaction product (Scheme 2B). The role of water in the reaction is currently under investigation. In this context, a water facilitated photolysis of perfluoroalkyl iodides via halogen bonding has been recently reported.^[33]

To demonstrate the scalability of the methodology herein reported, the fluoroalkylation of DB24 C8 was carried out on a gram-scale affording 65% (0,98 g) isolated yield of product **16** (see SI for details). The utility of the methodology is further highlighted by the post-synthetic fluoroalkylation of a mechanically interlocked molecule (MIM)^[34] such as [2]rotaxane **20**. Under the optimized reaction conditions and employing *n*-C₆F₁₃I as fluoroalkyl radical source, 50% yield of mono-perfluoroalkylated [2]rotaxane **21** was obtained (Scheme 3). We observed that (i) the reaction offered an exceptional chemo and regioselectivity, (ii) the mechanical bond did not affect the reactivity of DB24 C8 macrocycle encircled in the axle, and (iii) the interlocked architecture was preserved during the synthesis. From the experience gained along this work, it can be argued that the reaction of **20** could profit from the fact that the cavity in the crown is already complexed by the ammonium cation, enhancing the reactivity of the aromatic moiety towards the perfluoroalkyl radical attack in the aqueous phase. As a result of the incorporation of the ring-directing fluoroalkyl moiety, **21** is generated as a racemic mixture of two enantiomers that differ only for the 'orientation' of the macrocycle ring.^[35] However, the protocol's synthetic flexibility implies that the use of a chiral auxiliary, such as an enantiopure anion, may be considered to enable the direct diastereoselective synthesis of MIMs.



Scheme 2. Mechanistic studies and proposal.



Scheme 3. Post-synthetic perfluoroalkylation of [2]rotaxane 20.

Conclusions

A successful protocol for the late-stage incorporation of fluoroalkyl moieties into benzo crown ethers is reported. The photocatalyzed reactions are carried out in aqueous organic mixtures since the presence of water proved to be critical for yield maximization. The ability of crown ethers to complex metal ions was key to increase the substrates solubility in the reaction mixture hence facilitating perfluoroalkyl group substitution in high yields with exceptional chemo- and regioselectivity. The high selectivity towards monofunctionalization also for dibenzo crown ethers is particularly remarkable and fulfills one of the biggest synthetic challenges in late-stage crown ether functionalization. Fourteen new fluoroalkyl-substituted crown ethers were prepared and isolated in yields ranging from 60 to 99% in milligram to gram scale, thus proving the wide scope and easy scalability of this protocol. The R_F -substituted macrocyclic structures reported can have a direct application in the extraction of inorganic and organic cations in fluoruous phases, as phase transfer catalysts, and as fluoruous tags. Fluoroalkylated crown ethers have already proven their value in all these applications, but their usage has never taken off due to a lack of direct synthetic procedures, rendering them impractical. Furthermore, functionalized crown ethers can play an important role in the continuously growing field of molecular devices and machines. Indeed, as the functional complexity of nanoscale devices has increased, so has the demand for more diversity in the molecular structure of their constituents. We demonstrated that a rotaxane architecture can be directly perfluoroalkylated in high yield using the given approach, showcasing its potential to incorporate stereogenic and/or functional elements into mechanically interlocked structures with surprising ease and efficiency.

Experimental Section

In a 4 mL glass reaction vial provided with screw-cap septum and micro stir bar, substrate (0.2 mmol), N,N,N',N' -tetramethylethylenediamine (TMEDA, 3 equiv), Eosin Y (EY, 5 mol%), KCl, NaCl or LiCl (1.2 equiv) and 3 mL of solvent were introduced. When indicated, the mixture was purged with a stream of Ar for 10 minutes. Liquid fluorinated reagents (3 equiv) were introduced with

a microliter syringe. For Ar-purged reactions, a slight stream of Ar was passed through for 1 additional minute and then the vial was sealed. The closed reaction vessel was placed on a stir plate above the heat dissipator and stirred vigorously for 20 hrs. (at 22 °C) under constant irradiation with high power green LEDs (3 Watts, $\lambda_{max} = 525 \text{ nm} \pm 2 \text{ nm}$). After irradiation, the mixture was extracted thrice with $\text{CH}_2\text{Cl}_2/\text{water}$. The organic layers were gathered and dried over anhydrous Na_2SO_4 , filtered and evaporated under vacuo. The crude reaction mixture was purified by silica-gel (60 mesh) column chromatography, with the eluents indicated in the TLC conditions (see SI for details).

Supporting Information

Additional references cited within the Supporting Information.^[36–40]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: crown compounds · fluoroalkylation · photocatalysis · rotaxanes · water chemistry

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