

1,2,4-Triazolium Ions as Flexible Scaffolds for the Construction of Polyphilic Ionic Liquid Crystals

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1. First synthetic pathway to approach the ANRORC reaction

The originally proposed scheme provided for testing the ANRORC reaction on the alkylated oxadiazole **8** of Fig. S1.

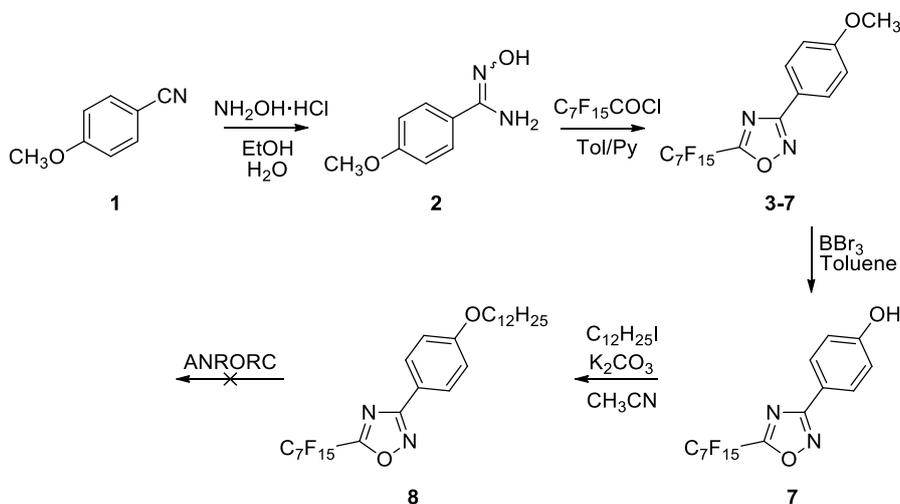


Fig. S1. First synthetic pathway to approach the ANRORC reaction

The synthetic process was carried out starting from 4-methoxybenzonitrile (**1**), which was reacted with hydroxylamine under reflux on aqueous ethanol solution, obtaining the corresponding amidoxime (**2**). The latter was subsequently reacted with perfluorooctanoyl chloride in toluene, using pyridine as a base to activate the oxadiazole cyclisation. The Williamson alkylation was conducted after the cleavage of the methoxy group (by boron tribromide in toluene under reflux) and proceeded in good yield in acetonitrile using potassium carbonate as the base and alkyl iodides or bromides as alkylating reagents (Fig. S1). Subsequently, the ANRORC transformation was tested, dissolving **8** in DMF and adding 5 and 10 mol. eq. of methyl hydrazine. Despite trying the reaction under several conditions, including at high temperature, the overcome could not be isolated. Probably oxadiazole **8** is not a good substrate for ANRORC reactions, which could be due to the long alkyl-chains, which kinetically hinder the ring closure of the reaction.

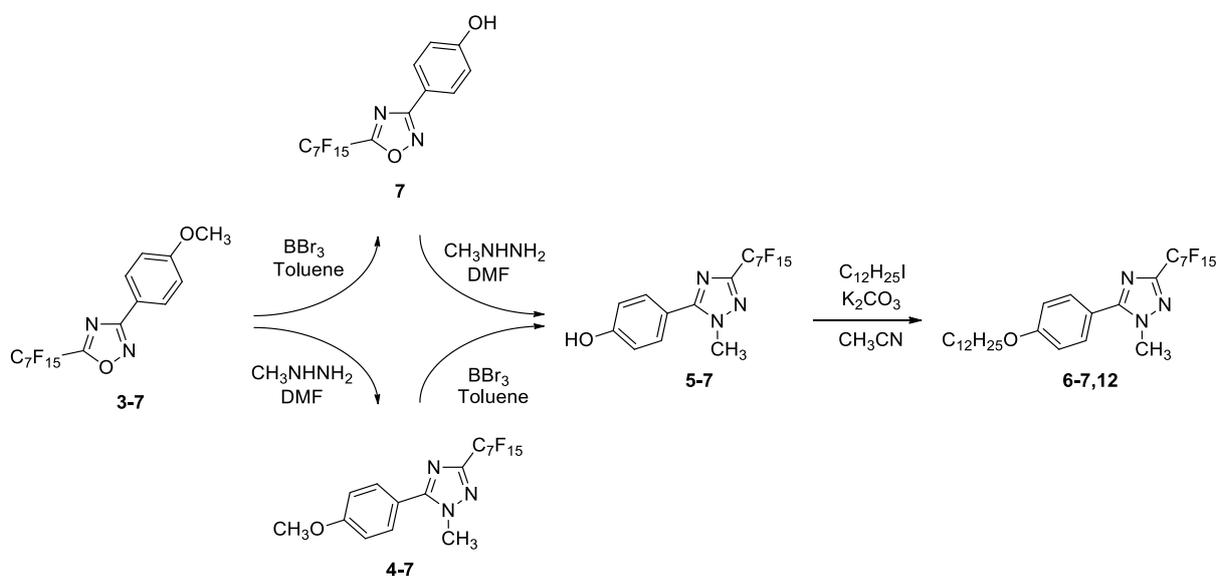


Fig. S2. Different pathways to obtain triazole **5-7** from oxadiazole **3-7**.

For this reason, the ANRORC reaction was moved to an earlier place in the synthesis scheme, leading the transformation into triazole from the simpler oxadiazole systems. So, the ANRORC chemistry can be performed either on compound **3-7** or **7** as well as both synthesis strategy has been tested and work fine (Fig. S2). But the pathway going through compound **4-7** shows higher yield, which was further enhanced (up to 85%) by carrying out the reaction at 110 °C.

2. Thermogravimetric analysis

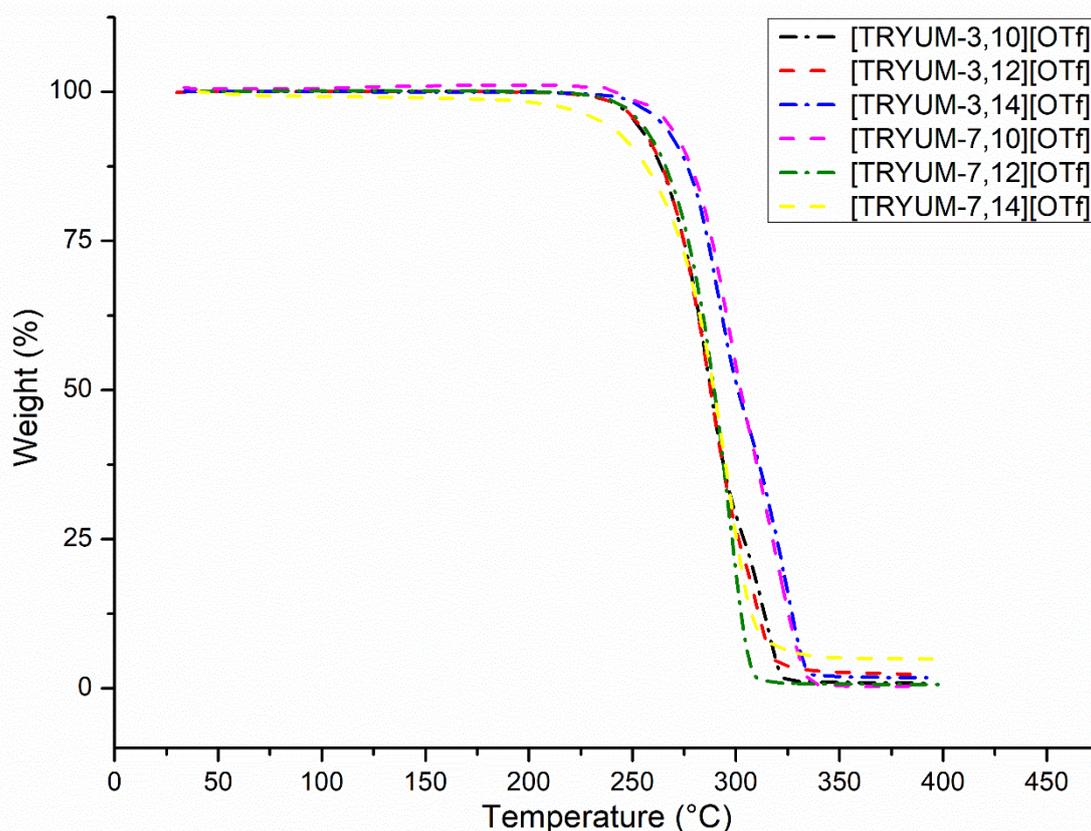


Fig. S3. Thermogravimetric analysis (TGA) of [TRYUM-*m,n*][OTf].

TGA analysis showed that the triazolium salts have good thermal stabilities, with little change in weight below 200 °C. Degradation temperatures are reported in Table S1.

Table S1. Thermal properties of [TRYUM-*m,n*][OTf] obtained by TGA.

Entry	m = 3, n=10	m = 3, n=12	m = 3, n=14	m = 7, n=10	m = 7, n=12	m = 7, n=14
T_{di} [°C]	266	266	273	273	275	270
T_{d10} [°C]	261	261	273	273	274	251
T_{df} [°C]	321	317	333	333	306	308

T_{di} and T_{df} are respectively the initial and final temperatures of degradation obtained from the onset values, while T_{d10} is the temperature at 10% weight loss.

3. Material and methods

Flash chromatography was performed using silica gel (200 – 400 mesh) and mixtures of ethyl acetate and light petroleum (fraction boiling in the range 40 – 60°C) in various ratios as eluents. All other starting materials and solvents were purchased from standard commercial sources and were used without further purification. No protective atmosphere was required during the synthesis unless stated otherwise.

Solution-state NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^1H), 376 MHz (^{19}F) as solutions in CDCl_3 or CD_3CN , unless stated otherwise.

CHN analysis were carried out on an Exter Analytical Inc. CE-440 Elemental Analyzer.

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hot-stage controlled by a Mettler FP90 central processor. Photomicrographs were captured via an InfinityX-21 MP digital camera mounted atop the microscope. Images were recorded at a magnification of 100x, and 200x during heating and cooling of the samples which were placed between two cover slips. Heating and cooling rates were 0.1 – 10 K min^{-1} .

Differential scanning calorimetry parameters were determined on a Mettler DSC822^e thermal analyser fitted with an autosampler operating with Mettler Stare software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, $\Delta H = 28.45 \pm 0.40$ J g^{-1}). Samples were prepared in 40 μL aluminium light crucibles, using an XS105 as analytical balance, and analysis were carried out with a rate of 10 °C min^{-1} for each sample under a N_2 flux of 60 $\text{cm}^3 \text{min}^{-1}$.

Thermogravimetric analysis were carried out by using the instrument Q5000 IR (TA Instruments) under nitrogen flow (25 $\text{cm}^3 \text{min}^{-1}$) by heating the samples from room temperature to 400 °C. Each sample (2 – 8 mg) was placed in a platinum pan and heated under the temperature program of 20 °C min^{-1} . The processed experimental data allowed us to calculate the initial (T_{di}) and the final (T_{df}) temperatures of degradation as well as temperature at 10% weight loss (T_{d10}).

Platinum electrodes were used for the electrochemical characterisation of the triazolium ILs by electrochemical impedance spectroscopy. A platinum electrode with probe encased in borosilicate glass has been built. Round tubing was used to produce the probe, which has a 0.7 cm internal diameter, on which two 0.4 x 0.4 cm platinum plates were attached diametrically opposite each other using an epoxy adhesive with high temperature resistance. The structural performance of the adhesive is to 175 °C and this represented an important limit temperature, which excludes the investigation of some compounds or their phases. The top edges of the platinum plates were welded to platinum wires linked in turn to copper cables for connection to the potentiostat. Electrode probe and plates sizes provide a minimum operating volume not over 0.112 mL. Secondly, a bigger size of round tubing has been used to produce a flat-bottomed sample holder, which fits perfectly the probe size. A thermal-block able to heat the sample holder of the electrode probe was produced. The heating system consists of an aluminium and brass block, where an electrical resistance heater and a temperature sensor have been inserted and these have been linked in turn to a temperature controller. The dependence of conductivity from the electrochemical cell potential was investigated using a computer-controlled potentiostat (SP-150 with EC-Lab[®] software package) through impedance measurements. The electrodes were used without additional polishing. The active area of the electrodes was determined with conductivity standard solutions (12880 and 5000 $\mu\text{S cm}^{-1}$) and already known ILs before impedance measurements. The ILs used as references were dodecyl-methylimidazolium bis(trifluoromethanesulfonyl) imide ($[\text{C}_{12}\text{mim}][\text{Tf}_2\text{N}]$) and ethyl-methylimidazolium

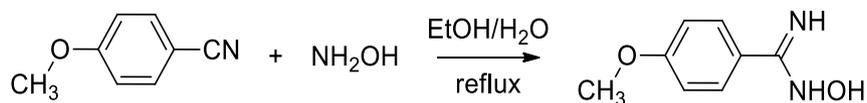
bis(trifluoromethanesulfonyl) imide ([C₂mim][Tf₂N]), whose conductivities are reported in the literature. The cell constant (k_c) of the probe was calculated from the measured resistance (R_1) and conductivity (σ) of the reference solutions, using the second Ohm's law. Measured k_c values are reproducible and reasonably comparable with k_c values calculated from the plates dimensions. Samples and references have been measured after equilibration at the desired temperature. Each measurement has been recorded with an AC potential amplitude of 120, 240, 300, 400 or 500 mV and over a frequency window from 1.0 Hz to 1 MHz. Impedance spectra were measured at the following polarisation potential: -10 V. Samples were analysed within LC and/or isotropic phases over a range of temperatures, collecting 4 or 5 points of conductivity/temperature in the sample phases. Conductivity values are always calculated by Ohm's law from the relative measured resistances, which are extrapolated from the Nyquist plot by fitting to a model of an equivalent circuit, whose relation in function of impedance is reported in equation (1),

$$Z(f) = \frac{R_1(1 + (i2\pi f)^{\alpha_1}Q_1R_2 + (i2\pi f)^{\alpha_2}Q_2R_2)}{1 + (i2\pi f)^{\alpha_2}Q_2R_2 + (i2\pi f)^{\alpha_1}Q_1(R_2 + R_1(1 + (i2\pi f)^{\alpha_2}Q_2R_2))} \quad (1)$$

where $\alpha_1 = \alpha_2$; i is an imaginary number; R_1 , Q_1 and Q_2 are resistances of the resistor and constant phase elements respectively of the equivalent circuit as well as R_2 , which represents the resistance made by the analysed material. All EIS measurements were carried out at atmospheric pressure in air on samples that had been stored in air. As such, it can be assumed that the samples are at equilibrium with atmospheric moisture, although TGA analysis (above) suggests low water contents for each sample. Presumably as all are crystalline solids under the storage conditions.

4. Synthesis and characterisation

4.1 Procedure for the synthesis of compound 2

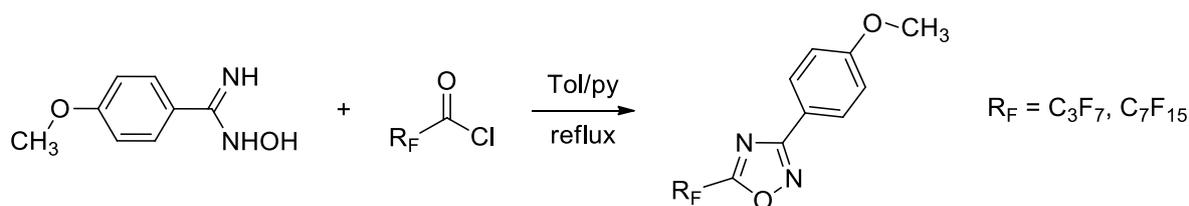


4-Methoxybenzonitrile (4.100 g; 30.79 mmol) was dissolved in EtOH (60 mL) in a 250 mL round-bottomed flask. Separately NaOH (2.460 g; 2.0 mol eq.) was dissolved in an amount of water as small as possible in another flask, using ice to help the dissolution, and NH₂OH·HCl (4.280 g; 2.0 mol eq) was added. The solutions were blended together and heated under reflux for 6 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). Ethanol was removed under vacuum, water (100 mL) was added and the precipitate was filtered under vacuum, washing with cold water. The Z-isomer was isolated by chromatography using petroleum ether and ethyl acetate 1:2. Yield = 55%.

(Z)-N'-Hydroxy-4-methoxybenzimidamide

Colourless solid. ¹H NMR (400 MHz, DMSO) δ : 9.49 (s, 1H), 7.62 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.73 (s, 2H), 3.76 (s, 3H).

4.2 General procedure for the synthesis of compounds 3-*m*



N'-Hydroxy-4-methoxybenzimidamide (**2**) (2.450 g, 14.8 mmol) was dissolved in toluene (75 ml) in a 250 ml round-bottomed flask. Next pyridine (2 mL) and perfluorobutanoyl chloride or perfluorooctanoyl chloride (1.5 mol eq.) were added. The obtained solution was heated under reflux for 5 – 7 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 50:1). Following the reflux, the mixture was dried under vacuum, water (100 mL) was added, pH was adjusted to 4-5 with a dilute HCl solution and the organic compounds were extracted with ethyl acetate (3 x 40 mL). After this the organic phases were dried with Na₂SO₄ and compounds **3-3** and **3-7** were isolated by chromatography using petroleum ether/ethyl acetate 5:1 as eluents. Yields = 64 – 83%.

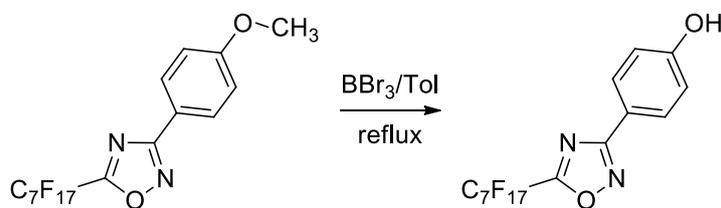
3-(4-Methoxyphenyl)-5-(perfluoropropyl)-1,2,4-oxadiazole (**3-3**)

Colourless solid. ¹H NMR (300 MHz, CDCl₃) δ : 8.07 (AA'XX', *J* = 8.9 Hz, 2H), 7.02 (AA'XX', *J* = 8.9 Hz, 2H, Ar), 3.89 (s, 3H).

3-(4-methoxyphenyl)-5-(perfluoroheptyl)-1,2,4-oxadiazole (**3-7**)

Colourless solid. ¹H NMR (400 MHz, CDCl₃) δ : 8.07 (AA'XX', *J* = 8.9 Hz, 2H), 7.02 (AA'XX', *J* = 8.9 Hz, 2H, Ar), 3.89 (s, 3H).

4.3 Procedure for the synthesis of compound 7

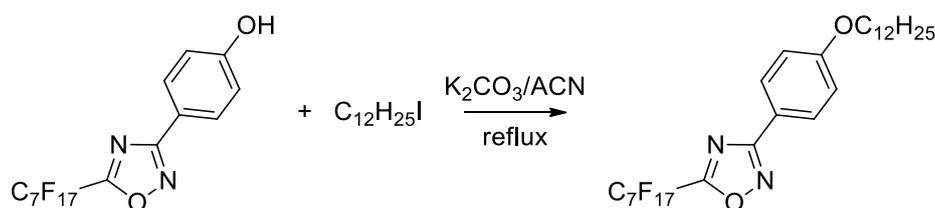


Oxadiazole **3-7** (0.12 g, 0.23 mmol) was dissolved in toluene (60 mL) in a 250 mL 3-neck round-bottomed flask and after this and BBr₃ in heptane (6 mL in each) were added. The mixtures were heated under reflux for 3.5 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). After this, water (15 mL) was added and the mixture was heated for another hour. After this the mixture was dried under vacuum, further water (50 mL) was added, pH was adjusted to neutral with a dilute NaOH solution and it was extracted with ethyl acetate (25 mL x 3). The organic phase was dried with Na₂SO₄ and the compounds **7** was isolated by chromatography using petroleum ether/ethyl acetate 5:1 and 2:1 as eluents. Yields = 74%

4-(5-(Perfluoroheptyl)-1,2,4-oxadiazol-3-yl)phenol (**3-7.1**)

Colourless solid. ¹H NMR (300 MHz, CDCl₃) δ : 7.59 (AA'XX', *J* = 8.8 Hz, 2H), 6.96 (AA'XX', *J* = 8.8 Hz, 2H), 5.84 (s, 1H).

4.4 Procedure for the synthesis of compound 8

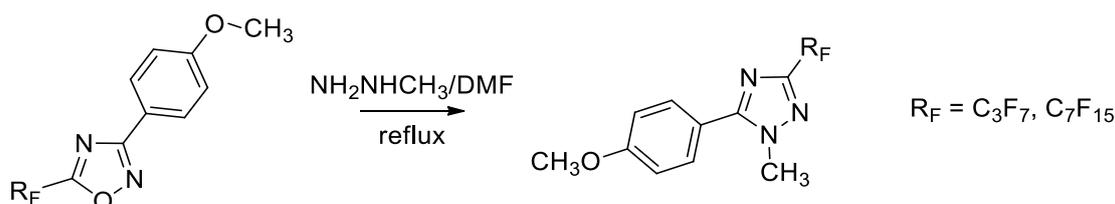


Oxadiazole **7** (0.11 g, 0.16 mmol) was dissolved in CH₃CN (15 mL) in a 100 mL round-bottomed flask as well as K₂CO₃ (3 mol eq.) and 1-bromododecane were added (1.5 mol eq.). The obtained mixture was heated at 80 °C for 6 h and after cooling, was dried under vacuum, water was added, pH was adjusted to neutral with a dilute HCl solution and the organic compounds were extracted with ethyl acetate (25 mL x 3). The organic phase was dried with Na₂SO₄ and the compounds **8** were isolated by chromatography using petroleum ether/ethyl acetate 20:1 and 5:1 as eluents. Yields = 89%.

3-(4-(Dodecyloxy)phenyl)-5-(perfluoroheptyl)-1,2,4-oxadiazole (3-7,12)

Colourless solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.64 (AA'XX', *J* = 8.6 Hz, 2H), 7.02 (AA'XX', *J* = 8.6 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 1.82 (p, *J* = 6.4 Hz, 2H), 1.57 – 1.10 (m, 18H), 0.88 (t, *J* = 6.5 Hz, 3H).

4.5 General procedure for the synthesis of compounds 4-*m*



The compounds **3-3** (2.700 g, 7.84 mmol) and **3-7** (2.700 g, 4.96 mmol) were dissolved separately in DMF (6 mL) in small round-bottomed flasks and methylhydrazine (5 mol eq.) was added to each tube. The solution was stirred and heated at 150 °C for 1.5-2.5 h and the reaction was monitored by TLC (petroleum ether/ethyl acetate 5:1). After cooling, water was added (100 mL), pH was adjusted to neutral with HCl solution and the organic compounds were extracted with diethyl ether (40 mL x 3). Then the organic phase was dried with Na₂SO₄ and the compounds **4-*m*** were isolated and purified by chromatography (using petroleum ether/ethyl acetate 5:1). Yields = 74-86%

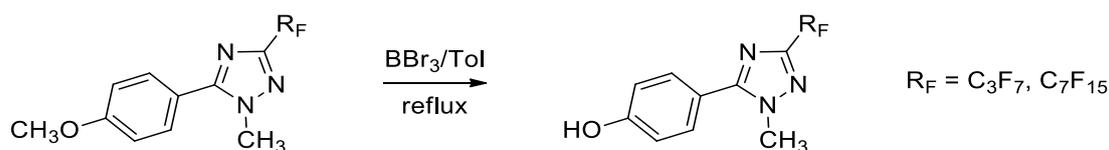
5-(4-Methoxyphenyl)-1-methyl-3-(perfluoropropyl)-1,2,4-triazole (4-3)

Colourless solid. ¹H NMR (300 MHz, CDCl₃) δ: 7.65 (AA'XX', *J* = 8.8 Hz, 2H), 7.04 (AA'XX', *J* = 8.8 Hz, 2H), 4.06 (s, 3H), 3.88 (s, 3H).

5-(4-Methoxyphenyl)-1-methyl-3-(perfluoroheptyl)-1,2,4-triazole (4-7)

Colourless solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (AA'XX', *J* = 8.8 Hz, 2H), 7.04 (AA'XX', *J* = 8.8 Hz, 2H), 4.06 (s, 3H), 3.88 (s, 3H).

4.6 General procedure for the synthesis of compounds 5-*m*



The triazoles **4-3** (2.500 g, 7.00 mmol) and **4-7** (2.500 g, 4.49 mmol) were separately degassed with three cycles vacuum and nitrogen in 250 mL 3-neck round-bottomed flasks and after this dried toluene (90 mL in each) and BBr_3 in heptane (6 mL in each) were added respectively by cannula under vacuum and by syringes. The mixture was heated under reflux for 3.5 h and the reactions were monitored by TLC (petroleum ether and ethyl acetate 5:1). After this, water was added (30 mL) to the mixtures which were heated for another hour. After cooling, the mixture was dried under vacuum, further water was added (70 mL), and the organic compounds were extracted with ethyl acetate (40 mL x 3). The organic phase was dried with Na_2SO_4 and the compounds **5-*m*** were isolated by chromatography using petroleum ether/ethyl acetate 5:1 and 2:1 as eluents. Yields = 87 – 94%

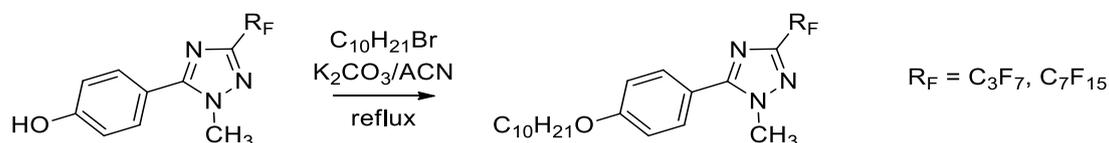
4-(1-Methyl-3-(perfluoropropyl)-1,2,4-triazol-5-yl)phenol (5-3)

Colourless solid. 1H NMR (300 MHz, $CDCl_3$) δ : 7.51 (AA'XX', $J = 7.8$ Hz, 2H), 7.09 (s, 1H), 6.86 (AA'XX', $J = 7.8$ Hz, 2H), 4.05 (s, 3H).

4-(1-methyl-3-(perfluoroheptyl)-1,2,4-triazol-5-yl)phenol (5-7)

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.59 (AA'XX', $J = 8.8$ Hz, 2H), 6.96 (AA'XX', $J = 8.8$ Hz, 2H), 5.84 (s, 1H), 4.06 (s, 3H).

4.7 General procedure for the synthesis of compounds 6-*m,10*



The triazoles **5-3** (0.70 g, 2.04 mmol) and **5-7** (0.70 g, 1.29 mmol) were dissolved separately in acetonitrile (10-15 mL) in 100 mL round-bottomed flasks as well as K_2CO_3 (3 mol eq.) and 1-bromodecane were added (2 mol eq.). The obtained mixture was heated at 80 °C for 6-14 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). After cooling, the mixture was dried under vacuum, water was added (50 mL), pH was adjusted to neutral with a diluted HCl solution and organic compounds were extracted with ethyl acetate (30 mL x 3). The organic phase was dried with $MgSO_4$ and the compounds **6-*m,10*** were isolated by chromatography using petroleum ether/ethyl acetate 20:1 and 5:1 as eluents. Yields = 87-97%.

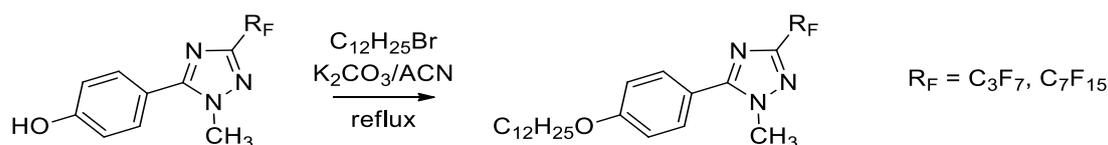
5-(4-(Decyloxy)phenyl)-1-methyl-3-(perfluoropropyl)-1,2,4-triazole (6-3,10)

Colourless solid. 1H NMR (300 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.4$ Hz, 2H), 6.96 (AA'XX', $J = 8.4$ Hz, 2H), 4.17 – 3.92 (m, 5H), 1.82 (p, $J = 6.4$ Hz, 2H, CH_2), 1.55 – 1.17 (m, 14H), 0.88 (t, $J = 5.5$ Hz, 3H, CH_3).

5-(4-(Decyloxy)phenyl)-1-methyl-3-(perfluoroheptyl)-1,2,4-triazole (6-7,10)

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.7$ Hz, 2H), 7.02 (AA'XX', $J = 8.7$ Hz, 2H), 4.12 – 3.91 (m, 5H), 1.82 (p, $J = 6.4$ Hz, 2H), 1.53 – 1.13 (m, 14H), 0.88 (t, $J = 6.6$ Hz, 3H).

4.8 General procedure for the synthesis of compounds 6-*m*,12



The triazoles **5-3** (0.70 g, 2.04 mmol) and **5-7** (0.70 g, 1.29 mmol) were dissolved separately in acetonitrile (10-15 mL) in 100 mL round-bottomed flasks as well as K_2CO_3 (3 mol eq.) and 1-bromododecane were added (2 mol eq.). The obtained mixture was heated at 80°C for 6-14 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). After cooling, the mixture was dried under vacuum, water was added (50 mL), pH was adjusted to neutral with a diluted HCl solution and organic compounds were extracted with ethyl acetate (30 mL x 3). The organic phase was dried with $MgSO_4$ and the compounds **6-*m*,12** were isolated by chromatography using petroleum ether/ethyl acetate 20:1 and 5:1 as eluents. Yields = 91-95%.

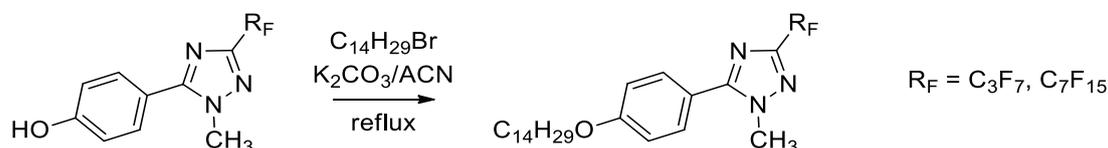
5-(4-(Dodecyloxy)phenyl)-1-methyl-3-(perfluoropropyl)-1,2,4-triazole (6-3,12)

Colourless solid. 1H NMR (300 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.3$ Hz, 2H), 6.96 (AA'XX', $J = 8.3$ Hz, 2H), 4.16 – 3.87 (m, 5H), 1.81 (p, $J = 6.4$ Hz, 2H), 1.55 – 1.17 (m, 18H), 0.88 (t, $J = 5.7$ Hz, 3H).

5-(4-(Dodecyloxy)phenyl)-1-methyl-3-(perfluoroheptyl)-1,2,4-triazole (6-7,12)

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.6$ Hz, 2H), 7.02 (AA'XX', $J = 8.6$ Hz, 2H), 4.06 (s, 3H), 4.02 (t, $J = 6.5$ Hz, 2H), 1.82 (p, $J = 6.4$ Hz, 2H), 1.57 – 1.10 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H).

4.9 General procedure for the synthesis of compounds 6-*m*,14



The triazoles **5-3** (0.70 g, 2.04 mmol) and **5-7** (0.70 g, 1.29 mmol) were dissolved separately in acetonitrile (10-15 mL) in 100 mL round-bottomed flasks as well as K_2CO_3 (3 mol eq.) and 1-bromotetradecane were added (2 mol eq.). The obtained mixture was heated at 80°C for 6-14 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). After cooling, the mixture was dried under vacuum, water (50 mL) was added, pH was adjusted to neutral with a diluted HCl solution and organic compounds were extracted with ethyl acetate (30 mL x 3). The organic phase was dried with $MgSO_4$ and the compounds **6-*m*,14** were isolated by chromatography using petroleum ether/ethyl acetate 20:1 and 5:1 as eluents. Yields = 83 – 96%.

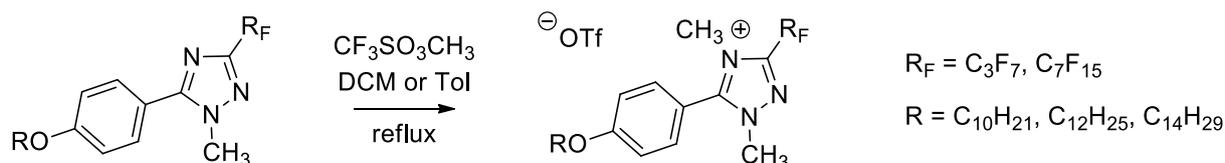
1-Methyl-3-(perfluoropropyl)-5-(4-(tetradecyloxy)phenyl)-1,2,4-triazole (6-3,14)

Colourless solid. 1H NMR (300 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.8$ Hz, 2H), 7.02 (AA'XX', $J = 8.8$ Hz, 2H), 4.06 (s, 3H), 4.02 (t, $J = 6.5$ Hz, 2H), 1.81 (p, $J = 6.4$ Hz, 2H), 1.55 – 1.18 (m, 22H), 0.88 (t, $J = 6.6$ Hz, 3H).

1-Methyl-3-(perfluoroheptyl)-5-(4-(tetradecyloxy)phenyl)-1,2,4-triazole (6-7,14)

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.64 (AA'XX', $J = 8.7$ Hz, 2H), 7.02 (AA'XX', $J = 8.7$ Hz, 2H), 4.05 (s, 3H), 4.01 (t, $J = 6.5$ Hz, 2H), 1.81 (p, $J = 6.4$ Hz, 2H), 1.57 – 1.13 (m, 22H), 0.88 (t, $J = 6.7$ Hz, 3H).

4.10 General procedure for the synthesis of triazolium triflates [TRYUM-*m,n*][OTf]



The triazoles **6-*m,n*** were separately dissolved in toluene in small round-bottomed flasks and $CF_3SO_3CH_3$ (15 mol eq.) was added. The mixture was stirred and heated at 60 °C for total 4-6 h. The reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1 and 1:1). After cooling, water (50 mL) was added at the mixture, which was dried, pH was adjusted to neutral, and the organic compounds were extracted with DCM (30 mL x 3). The organic phase was dried with $MgSO_4$ and the compounds [TRYUM-*m,n*][OTf] were isolated by chromatography using petroleum ether / ethyl acetate 5:1 and 1:1 as eluents. Yields = 76 – 92%.

5-(4-(Decyloxy)phenyl)-1,4-dimethyl-3-(perfluoropropyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-3,10][OTf])

Colourless solid. 1H NMR (300 MHz, CD_3CN) δ : 7.64 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 7.26 (AA'XX', $J = 8.9$ Hz, 2H), 4.13 (t, $J = 6.5$ Hz, 2H), 4.00 (s, 3H), 3.80 (s, 3H), 1.80 (p, $J = 6.4$ Hz, 2H), 1.52 – 1.30 (m, 14H), 0.89 (t, $J = 6.4$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.56 (s), -79.63 (t, $J = 10.0$ Hz), -109.51 – -112.48 (m), -123.91 – -125.61 (m). Anal. Calcd. for $C_{24}H_{31}F_{10}N_3O_4S$: C, 44.51; H, 4.83; N, 6.49. Found: C, 44.21; H, 4.89; N, 6.33.

5-(4-(Dodecyloxy)phenyl)-1,4-dimethyl-3-(perfluoropropyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-3,12][OTf])

Colourless solid. 1H NMR (300 MHz, CD_3CN) δ : 7.66 (AA'XX', $J = 8.9$ Hz, 2H), 7.28 (AA'XX', $J = 8.9$ Hz, 2H), 4.15 (t, $J = 6.5$ Hz, 2H), 4.03 (s, 3H), 3.83 (s, 3H), 1.84 (p, $J = 6.4$ Hz, 2H), 1.62 – 1.21 (m, 18H), 0.91 (t, $J = 6.6$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.56 (s), -79.63 (t, $J = 10.0$ Hz), -109.51 – -112.48 (m), -123.91 – -125.61 (m). Anal. Calcd. for $C_{26}H_{35}F_{10}N_3O_4S$: C, 46.22; H, 5.22; N, 6.22. Found: C, 46.06; H, 5.19; N, 6.18.

1,4-Dimethyl-3-(perfluoropropyl)-5-(4-(tetradecyloxy)phenyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-3,14][OTf])

Colourless solid. 1H NMR (300 MHz, CD_3CN) δ : 7.63 (AA'XX', $J = 8.9$ Hz, 2H), 7.26 (AA'XX', $J = 8.9$ Hz, 2H), 4.13 (t, $J = 6.5$ Hz, 2H), 4.00 (s, 3H), 3.80 (s, 3H), 1.81 (p, $J = 6.4$ Hz, 2H), 1.59 – 1.21 (m, 22H), 0.88 (t, $J = 6.6$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.56 (s), -79.63 (t, $J = 10.0$ Hz), -109.51 – -112.48 (m), -123.91 – -125.61 (m). Anal. Calcd. for $C_{28}H_{39}F_{10}N_3O_4S$: C, 47.79; H, 5.59; N, 5.97. Found: C, 47.71; H, 5.90; N, 5.41.

5-(4-(Decyloxy)phenyl)-1,4-dimethyl-3-(perfluoroheptyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-7,10][OTf])

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.80 (AA'XX', $J = 8.4$ Hz, 2H), 7.16 (AA'XX', $J = 8.4$ Hz, 2H), 4.21 – 3.97 (m, 5H), 3.88 (s, 3H), 1.84 (p, $J = 6.4$ Hz, 2H), 1.94 – 1.74 (m, 14H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.56 (s), -80.69 (t, $J = 9.9$ Hz), -110.21 (s), -120.23 (s), -121.06 (s), -121.81 (s), -122.60 (s), -126.06 (s). Anal. Calcd. for $C_{28}H_{31}F_{18}N_3O_4S$: C, 39.68; H, 3.69; N, 4.96. Found: C, 39.57; H, 3.63; N, 4.88.

5-(4-(Dodecyloxy)phenyl)-1,4-dimethyl-3-(perfluoroheptyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-7,12][OTf])

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.80 (AA'XX', $J = 8.9$ Hz, 2H), 7.13 (AA'XX', $J = 8.9$ Hz, 2H), 4.22 – 3.91 (m, 5H), 3.83 (s, 3H), 1.81 (p, $J = 6.4$ Hz, 2H), 1.62 – 1.21 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.65 (s), -80.79 (t, $J = 9.9$ Hz), -110.40 (s), -120.27 (s), -121.16 (s), -121.89 (s), -122.68

(s), -126.16 (t, $J = 14.9, 7.0$ Hz). Anal. Calcd. for $C_{30}H_{35}F_{18}N_3O_4S$: C, 41.15; H, 4.03; N, 4.80. Found: C, 41.43; H, 4.09; N, 4.64.

1,4-Dimethyl-3-(perfluoroheptyl)-5-(4-(tetradecyloxy)phenyl)-1,2,4-triazol-4-ium trifluoromethanesulfonate ([TRYUM-7,14][OTff])

Colourless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 7.80 (AA'XX', $J = 8.2$ Hz, 2H), 7.15 (AA'XX', $J = 8.2$ Hz, 2H), 4.06 – 4.04 (m, 5H), 3.86 (s, 3H), 1.85 (p, $J = 6.4$ Hz, 2H), 1.46 – 1.21 (m, 22H), 0.87 (t, $J = 6.6$ Hz, 3H, CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ : -78.58 (s), -80.69 (t, $J = 9.9$ Hz), -110.21 (s), -120.23 (s), -121.07 (s), -121.81 (s), -122.60 (s), -126.08 (t, $J = 14.9, 7.0$ Hz). Anal. Calcd. for $C_{32}H_{39}F_{18}N_3O_4S$: C, 42.53; H, 4.35; N, 4.65. Found: C, 42.35; H, 4.24; N, 4.65.

5. Single crystal X-ray data

Crystal data and structure refinement for [TRYUM-7,10][OTf].

Identification code	[TRYUM-7,10][OTf]
Empirical formula	$C_{28}H_{31}F_{18}N_3O_4S$
Formula weight	847.62
Temperature/K	110.05(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.8350(8)
b/Å	8.0827(3)
c/Å	22.8945(9)
$\alpha/^\circ$	90
$\beta/^\circ$	96.376(4)
$\gamma/^\circ$	90
Volume/Å ³	3463.9(3)
Z	4
ρ_{calc}/cm^3	1.625
μ/mm^{-1}	2.102
F(000)	1720.0
Crystal size/mm ³	0.326 × 0.105 × 0.022
Radiation	CuK α ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	7.772 to 134.158
Index ranges	$-22 \leq h \leq 21, -8 \leq k \leq 9, -19 \leq l \leq 27$
Reflections collected	17893
Independent reflections	6188 [$R_{int} = 0.0319, R_{sigma} = 0.0326$]
Data/restraints/parameters	6188/57/575
Goodness-of-fit on F^2	1.041
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0485, wR_2 = 0.1245$
Final R indexes [all data]	$R_1 = 0.0610, wR_2 = 0.1359$
Largest diff. peak/hole / e Å ⁻³	0.66/-0.66

Data collected and processed by Adrian C Whitwood