Functionalization of *s*-tetrazine: Preparation of new compounds with high synthetic potential

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Abstract: Application of thiol-ene chemistry on chloro-allyloxy-tetrazine shows an incompatibility of the *s*-tetrazine ring with radical addition. Thus, in order to synthesize new dialkoxy-*s*-tetrazines including a fluorinated substituent, thiol was added across allylalcohol and the resulting intermediate was then allowed to react with dichloro-*s*-tetrazine. Subsequent substitution on the second chlorine leads to disubstituted derivatives.

Keywords: Radical addition, fluorine, tetrazine, thiol

Résumé: L'application de la chimie du thiol-ène au chloro-allyloxy-tétrazine montre une incompatibilité du noyau tétrazinique aux additions radicalaires. Ainsi, afin de synthétiser de nouvelles dialkoxy-*s*-tétrazines incluant des substituents fluorés, des thiols sont additionnés à l'alcool allylique et l'intermédiaire résultant réagit ensuite avec la dichloro-*s*-tétrazine. La substitution du second chlore conduit aux dérivés disubstitués.

Mots clés: Addition radicalaire, fluor, tétrazine, thiol

INTRODUCTION

The physico-chemical [1-14] or biological [15-19] characteristics owned by *s*-tetrazine give a particular importance to this heterocyclic compound. This aromatic derivative has been shown to be an efficient building block for new functionalized molecules and molecular materials synthesis [20].

s-Tetrazines are strongly fluorescent molecules [1-8] and this places them among the smallest organic fluorophores in the visible range [8]. Besides, they could be electrochemically reduced to a stable anion -radical in solution [1-14]. Thus, electrochemical fluorescence switching of these molecules was largely investigated [2,5,6,13,14]. Furthermore, *s*-tetrazines offer distinct advantages in energetic materials field [21] and due to their high electro-attractor effect, they can be used in solar cells [22]. Otherwise, *s*-tetrazine and derivatives offer a broad array of biological activities, e. g. anti-cancer [15,16], anti-inflammatory [17], anti-viral [18] and insecticidal [19].

On the other hand, use of thiol-ene click chemistry [23-26] is widely spread since the few last years. This highly efficient and orthogonal reaction allows access to several functional materials such as block copolymers [27], cross-linked materials and dendrimers [28]. Recently, the synthetic potential of thiol-ene click chemistry is exploited to obtain a multitude of thin-film systems [24], modify backbone of polyoxazolines and polybutadiene [29] and build glycodendrons [30].

Several mono- and disubstituted *s*-tetrazines are described in the literature [1-8,12-14]. Benefiting from the easy access to the basic synthon dichloro-*s*-tetrazine [31,32], we describe herein the synthesis of new fluorinated *s*-tetrazines using an interesting synthetic way.

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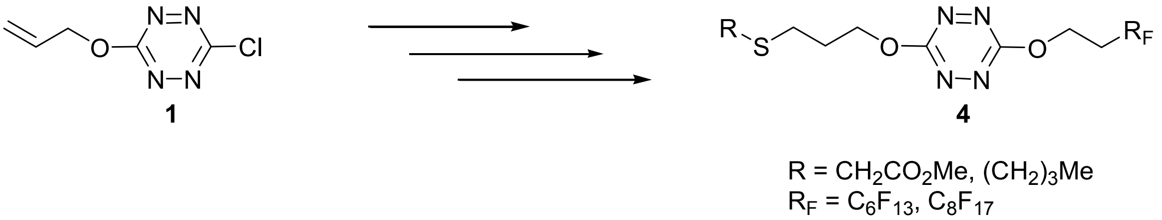
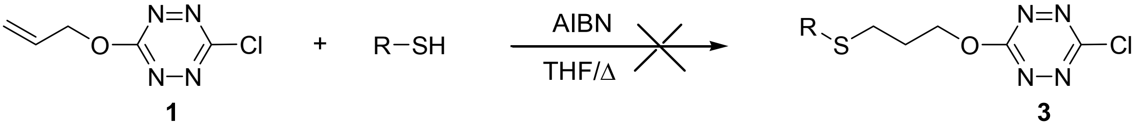


Scheme 1: Synthetic route to aimed tetrazine **4**



Scheme 2: Attempted synthesis of monosubstituted *s*-tetrazine **3**

RESULTS AND DISCUSSION

Starting from chloro-allyloxy-tetrazine **1,** we have considered the synthesis of the fluorinated analogues **4**, in which R may be an alkyl group or a linker for further conjugates as summarized in Scheme 1.

In a first attempt, we tried the synthesis of *s*-tetrazine **3** by radical addition of thiol on chloro-allyloxy-tetrazine **1**, according to thiol-ene chemistry [23] believing that the adduct **3** such obtained could then react with 2-*F*-alkylethanol to give *s*-tetrazine **4**.

Unfortunately, we faced the problem of incompatibility of the *s*-tetrazine ring with radical reaction. Indeed, treatment of compound **1** by thiol under radical conditions leads to the disappearance of the deep red color of the solution (Scheme 2), which indicates that the tetrazinic cycle has been destroyed.

Incompatibility of the *s*-tetrazine ring with radical reactions was also confirmed by compounds **5** [1] and **6** illustrated in the figure below, which were destroyed when submitted to the same radical treatment.

As an alternative, the chloro-alkoxy-tetrazine **3** was prepared in two steps, (i) thiol and allylalcohol reacted in the presence of AIBN [23] and (ii), the resulting ω-hydroxysulfide **2** was submitted to dichloro-*s*-tetrazine treatment catalyzed by 2,4,6-collidine [1-4], to furnish compound **3** in good yield, as a deep red viscous oil (Scheme 3).

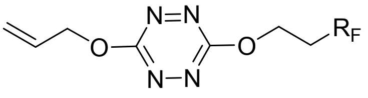
Chloro-alkoxy-tetrazine **3** was then converted into the targeted fluorinated derivative **4** gathered in Scheme 4.

Whereas the base 2,4,6-collidine was sufficient to induce S_NAr of one chlorine of dichloro-*s*-tetrazine, the substitution of the remained chlorine was more difficult and a stronger base (sodium hydride) [4] was necessary to convert compound **3** into the disubstituted analogue **4**.

The prepared *F*-alkyl-dialkoxy-tetrazine **4** could present some interesting electrochemical properties and fluorescence skills. They also may find applications in variable fields and developing new materials such as realization of new sensors for pollutants detection.

CONCLUSIONS

Radical addition of thiol on unsaturated *s*-tetrazine leads to destruction of tetrazinic cycle proved by the discoloration of the mixture firstly red. In order to prepare disubstituted *s*-tetrazines



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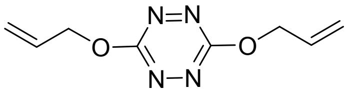

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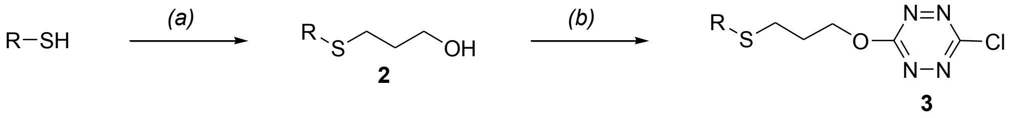
$R_F = C_6F_{13}, C_8F_{17}$

Figure: Compounds **5** and **6** submitted to radical addition



3	R	Yield (%)
a	CH_2CO_2Me	77
b	$(CH_2)_3Me$	65

(a) Allylalcohol, AIBN, THF, 75°C; *(b)* Dichloro-*s*-tetrazine, 2,4,6-collidine, CH_2Cl_2, rt

Scheme 3: Synthetic pathway of chloro-alkoxy-tetrazine **3**

with partially fluorinated *O*-alkyl substituents, the radical addition was accomplished separately on allylic alcohol. The obtained ω-hydroxysulfide was then introduced on *s*-tetrazine moiety by aromatic nucleophilic substitution. Finally, a second substitution leads to the desired product when applied on perfluorinated alcohol.

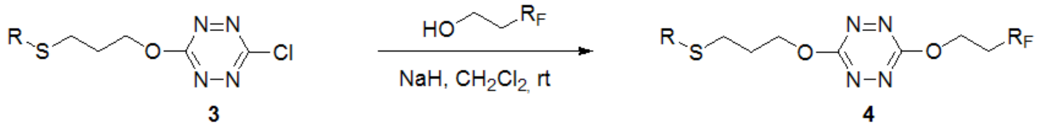
EXPERIMENTAL

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ at 25°C on a JEOL ESC-400 MHz spectrometer at 400, 100 and 376 MHz respectively using the TMS as an internal reference (δ = 0.00) for ^{1}H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR. IR spectra were recorded on Nicolet-Avatar 330 FT-IR spectrometer. Monitoring of the reaction course and purity of the compounds prepared are carried out using TLC on percolated silica gel GF254 (10~40µ) plates with detection by UV. Melting points are measured with Kofler apparatus. Dichloro-*s*-tetrazine is prepared as described in literature [4]. The abbreviation Tz refers to tetrazine.

1. Radical Addition: General Method

A solution of allylalcohol (1 eq.), AIBN (0.1-0.25 mmol) and thiol (1 eq.) in dry THF ($c \approx 0.1$ M) was thoroughly degassed (N_2) before reacted at 75°C. After stirring for 1-4 h (TLC control), the reaction was concentrated and the obtained residue was then subject to flash chromatography (petroleum ether / EtOAc 4:1) to yield the *ω*-hydroxysulfide **2**.

Methyl 2-(3-hydroxypropylthio)acetate (2a). Yield: 57%. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 3.58 (s, 3H, CH_3), 3.53 (t, 2H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, HO−$C\mathit{H}_2$ $(CH_2)_2S$), 3.10 (s, 2H, S–CH_2−C=O), 2.57 (t, 2H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $HO(CH_2)_2C\mathit{H}_2$−S), 1.67 (m, 2H, HO−$CH_2C\mathit{H}_2CH_2$−S). ^{13}C NMR ($CDCl_3$): *δ* (ppm) 171.1 (C=O), 60.5 (HO−$\underline{C}H_2(CH_2)_2S$), 52.2 ($CH_3$), 33.2 (S–$\underline{C}H_2$−C=O), 31.3 (HO−$CH_2\underline{C}H_2CH_2$−S), 28.9 ($HO(CH_2)_2\underline{C}H_2$−S). Elem. Anal. Calcd for



4	R	R_F	Yield (%)	M. p. (°C)
a	CH_2CO_2Me	C_6F_{13}	71	Viscous oil
b	CH_2CO_2Me	C_8F_{17}	73	58
c	$(CH_2)_3Me$	C_6F_{13}	78	Viscous oil
d	$(CH_2)_3Me$	C_8F_{17}	75	86

Scheme 4: Synthesis of *F*-alkyl-dialkoxy-tetrazine **4**

$C_6H_{12}O_3S$: C, 43.88; H, 7.37; S, 19.53. Found: C, 43.86; H, 7.31; S, 19.64.

3-(Butylthio)propan-1-ol (2b).

Yield: 76%. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.58 (m, 2H, $HO{-}C\mathit{H}_2(CH_2)_2S$), 2.49 (m, 2H, $HO{-}CH_2C\mathit{H}_2CH_2{-}S$), 2.41 (m, 2H, $HO(CH_2)_2C\mathit{H}_2{-}S$), 1.71 (m, 2H, $CH_3(CH_2)_2C\mathit{H}_2{-}S$), 1.45 (m, 2H, $CH_3CH_2C\mathit{H}_2CH_2{-}S$), 1.28 (m, 2H, $C\mathit{H}_2{-}CH_3$), 0.79 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 61.2 ($HO{-}\underline{C}H_2(CH_2)_2S$), 31.8 ($HO{-}CH_2\underline{C}H_2CH_2{-}S$), 31.6 ($HO(CH_2)_2\underline{C}H_2{-}S$), 31.5 ($CH_3(CH_2)_2\underline{C}H_2{-}S$), 28.5 ($CH_3CH_2\underline{C}H_2CH_2{-}S$), 21.8 ($\underline{C}H_2{-}CH_3$), 13.6 ($CH_3$). Elem. Anal. Calcd for $C_7H_{16}OS$: C, 56.71; H, 10.88; S, 21.63. Found: C, 56.63; H, 10.81; S, 21.74.

2. Preparation of chloro-alkoxy-tetrazine (3a-b): General procedure

Dichloro-*s*-tetrazine (1 eq.) was reacted with ω-hydroxysulfide **2** (1 eq.) in dry CH_2Cl_2 ($c \approx 0.1$M). 2,4,6-Collidine (1.2 eq.) was added drop wise under N_2 and the reaction was stirred at room temperature for 1-2 h (TLC control). The solvent was removed and the obtained residue was purified by column chromatography (petroleum ether / EtOAc 2:3) to yield *s*-tetrazine **3**.

Methyl 2-(3-(6-chloro-1,2,4,5-tetrazin-3-yloxy) propylthio)acetate (3a).

Yield: 73%. Viscous oil. IR (neat): υ (cm^{-1}) 2922 (C−H), 1728 (C=O), 1485, 1457, 1439 (Tz), 1360 (C−S), 1280 (C−O). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.70 (t, 2H, $^3J_{H\text{-}H} = 6.4$ Hz, $O{-}C\mathit{H}_2(CH_2)_2S$), 3.66 (s, 3H, CH_3), 3.19 (s, 2H, $S{-}CH_2{-}C{=}O$), 2.82 (t, 2H, $^3J_{H\text{-}H} = 6.8$ Hz, $O(CH_2)_2C\mathit{H}_2{-}S$), 2.18 (m, 2H, $O{-}CH_2C\mathit{H}_2CH_2{-}S$). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.7 (C=O), 166.6 ($C_{Tz}{-}O$), 164.4 ($C_{Tz}{-}Cl$), 68.9 ($O{-}\underline{C}H_2(CH_2)_2S$), 52.5 ($CH_3$), 33.4 ($S{-}\underline{C}H_2{-}C{=}O$), 28.7 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 27.7 ($O(CH_2)_2\underline{C}H_2{-}S$). Elem. Anal. Calcd for $C_8H_{11}ClN_4O_3S$: C, 34.47; H, 3.98; N, 20.10; S, 11.50. Found: C, 34.53; H, 3.91; N, 20.28; S, 11.65.

3-(3-(Butylthio)propoxy)-6-chloro-1,2,4,5-tetrazine (3b).

Yield: 65%. Viscous oil. IR (neat): υ (cm^{-1}) 2930 (C−H), 1485, 1456 (Tz), 1357 (C−S). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.73 (m, 2H, $O{-}C\mathit{H}_2(CH_2)_2S$), 2.71 (m, 2H, $O{-}CH_2C\mathit{H}_2CH_2{-}S$), 2.49 (m, 2H, $O(CH_2)_2C\mathit{H}_2{-}S$), 2.18 (m, 2H, $CH_3(CH_2)_2C\mathit{H}_2{-}S$), 1.55 (m, 2H, $CH_3CH_2C\mathit{H}_2CH_2{-}S$), 1.37 (m, 2H, $C\mathit{H}_2{-}CH_3$), 0.88 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.7 ($C_{Tz}{-}O$), 164.4 ($C_{Tz}{-}Cl$), 69.3 ($O{-}\underline{C}H_2(CH_2)_2S$), 31.9 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 31.7 ($O(CH_2)_2\underline{C}H_2{-}S$), 28.4 ($CH_3(CH_2)_2\underline{C}H_2{-}S$), 28.1 ($CH_3CH_2\underline{C}H_2CH_2{-}S$), 22 ($\underline{C}H_2{-}CH_3$), 13.7 ($CH_3$). Elem. Anal. Calcd for $C_9H_{15}ClN_4OS$: C, 41.14; H, 5.75; N, 21.32; S, 12.20. Found: C, 41.26; H, 5.90; N, 21.58; S, 12.11.

3. Preparation of *F*-alkyl-dialkoxy-tetrazine (4a-d): General procedure

To a solution of *F*-alkylated alcohol (1 eq.) in dry CH_2Cl_2 ($c \approx 0.1$ M) thoroughly degassed (N_2) was added 10% excess of 60% NaH. To the formed *F*-alkylated alcoholate, a degassed solution of chloro-alkoxy-tetrazine **3** (1 eq.) in dry CH_2Cl_2 ($c \approx 0.1$ M) was added, and the mixture reacted at room temperature for about 1-4 h (TLC control). The solution was quenched with cold water and the organic layer was extracted with 3×30 mL of $CHCl_3$ and dried under Na_2SO_4. The residue after concentration was purified by column chromatography (*n*-pentane / EtO_2 4:1) yielding *F*-alkyl-dialkoxy-*s*-tetrazine **4**.

Methyl 2-(3-(6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)-1,2,4,5-tetrazin-3-yloxy) propylthio)acetate (4a).

Yield: 71%. Viscous oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.81 (t, 2H, $^3J_{H\text{-}H} = 6.8$ Hz, $O{-}C\mathit{H}_2(CH_2)_2S$), 4.62 (t, 2H, $^3J_{H\text{-}H} = 6.0$ Hz, $C_6F_{13}{-}CH_2C\mathit{H}_2$), 3.67 (s, 3H, CH_3), 3.19 (s, 2H, $S{-}CH_2{-}C{=}O$), 2.82 (t, 2H, $^3J_{H\text{-}H} = 7.2$ Hz, $O{-}CH_2C\mathit{H}_2CH_2{-}S$), 2.72 (m, 2H, $C_6F_{13}{-}CH_2$), 2.16 (m, 2H, $O(CH_2)_2C\mathit{H}_2{-}S$). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.7 (C=O), 166.2; 165.5 ($C_{Tz}{-}O$), 100-120 (C_6F_{13}), 68 ($O{-}\underline{C}H_2(CH_2)_2S$), 61.5 ($C_6F_{13}{-}CH_2\underline{C}H_2$), 52.4 ($CH_3$), 33.3 ($S{-}\underline{C}H_2{-}C{=}O$), 30.6 (t, $^2J_{C\text{-}F} = 21.75$ Hz, $C_6F_{13}{-}\underline{C}H_2$), 28.8 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 27.9 ($O(CH_2)_2\underline{C}H_2{-}S$). ^{19}F NMR ($CDCl_3$): δ (ppm) -80.88 (m, 3F, CF_3), -113.50 (m, 2F, $CF_{2\alpha}$), -121.96 (m, 2F, $CF_{2\beta}$), -122.97 (m, 2F, $CF_{2\gamma}$), -123.57 (m, 2F, $CF_{2\delta}$), -126.25 (m, 2F, $CF_{2\omega}$). Elem. Anal. Calcd for $C_{16}H_{15}F_{13}N_4O_4S$: C, 31.69; H, 2.49; N, 9.24; S, 5.29. Found: C, 31.73; H, 2.45; N, 9.33; S, 5.53.

Methyl 2-(3-(6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyloxy)-1,2,4,5-tetrazin-3-yloxy)propylthio)acetate (4b).

Yield: 73%. mp: 58°C. IR (neat): υ (cm^{-1}) 2921 (C−H), 1738 (C=O), 1484, 1441 (Tz), 1367 (C−S), 1283 (C−O), 1147-1201 (C−F). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.88 (t, 2H, $^3J_{H\text{-}H} = 6.4$ Hz, $O{-}C\mathit{H}_2(CH_2)_2S$), 4.69 (t, 2H, $^3J_{H\text{-}H} = 6.0$ Hz, $C_8F_{17}{-}CH_2C\mathit{H}_2$), 3.74 (s, 3H, CH_3), 3.26 (s, 2H, $S{-}CH_2{-}C{=}O$), 2.89 (t, 2H, $^3J_{H\text{-}H} = 6.8$ Hz, $O{-}CH_2C\mathit{H}_2CH_2{-}S$), 2.79

(m, 2H, $C_8F_{17}{-}CH_2$), 2.23 (m, 2H, $O(CH_2)_2CH_2{-}S$). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.8 (C=O), 166.4; 165.6 ($C_{Tz}{-}O$), 100-120 (C_8F_{17}), 68.3 ($O{-}\underline{C}H_2(CH_2)_2S$), 61.7 ($C_8F_{17}{-}CH_2\underline{C}H_2$), 52.5 ($CH_3$), 33.5 ($S{-}\underline{C}H_2{-}C{=}O$), 30.8 (t, $^2J_{C\text{-}F}$ = 21.9 Hz, $C_8F_{17}{-}\underline{C}H_2$), 29 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 28 ($O(CH_2)_2\underline{C}H_2{-}S$). ^{19}F NMR ($CDCl_3$): δ (ppm) -80.74 (m, 3F, CF_3), -113.40 (m, 2F, $CF_{2\alpha}$), -121.78 (m, 6F, $CF_{2\beta}CF_{2\gamma}CF_{2\delta}$), -122.67 (m, 2F, $CF_{2\varepsilon}$), -123.62 (m, 2F, $CF_{2\xi}$), -126.06 (m, 2F, $CF_{2\omega}$). Elem. Anal. Calcd for $C_{18}H_{15}F_{17}N_4O_4S$: C, 30.61; H, 2.14; N, 7.93; S, 4.54. Found: C, 30.50; H, 2.05; N, 7.99; S, 4.77.

3-(3-(Butylthio)propoxy)-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)-1,2,4,5-tetrazine (4c).
Yield: 78%. Viscous oil. IR (neat): υ (cm^{-1}) 2960 (C–H), 1482, 1443 (Tz), 1364 (C–S), 1143-1203 (C–F). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.83 (m, 2H, $O{-}CH_2(CH_2)_2S$), 4.64 (m, 2H, $C_6F_{13}{-}CH_2CH_2$), 2.72 (m, 4H, $C_6F_{13}{-}CH_2$, $O{-}CH_2CH_2CH_2{-}S$), 2.50 (m, 2H, $O(CH_2)_2CH_2{-}S$), 2.15 (m, 2H, $CH_3(CH_2)_2CH_2{-}S$), 1.53 (m, 2H, $CH_3CH_2CH_2CH_2{-}S$), 1.38 (m, 2H, $CH_2{-}CH_3$), 0.87 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.4; 165.6 ($C_{Tz}{-}O$), 100-120 (C_6F_{13}), 68.6 ($O{-}\underline{C}H_2(CH_2)_2S$), 61.6 ($C_6F_{13}{-}CH_2\underline{C}H_2$), 32 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 31.8 ($O(CH_2)_2\underline{C}H_2{-}S$), 30.8 (t, $^2J_{C\text{-}F}$ = 21.9 Hz, $C_6F_{13}{-}\underline{C}H_2$), 28.7 ($CH_3(CH_2)_2\underline{C}H_2{-}S$), 28.3 ($CH_3CH_2\underline{C}H_2CH_2{-}S$), 22 ($\underline{C}H_2{-}CH_3$), 13.7 ($CH_3$). ^{19}F NMR ($CDCl_3$): δ (ppm) -80.87 (m, 3F, CF_3), -113.52 (m, 2F, $CF_{2\alpha}$), -121.91 (m, 2F, $CF_{2\beta}$), -122.89 (m, 2F, $CF_{2\gamma}$), -123.50 (m, 2F, $CF_{2\delta}$), -126.13 (m, 2F, $CF_{2\omega}$). Elem. Anal. Calcd for $C_{17}H_{19}F_{13}N_4O_2S$: C, 34.58; H, 3.24; N, 9.49; S, 5.43. Found: C, 34.68; H, 3.18; N, 9.37; S, 5.56.

3-(3-(Butylthio)propoxy)-6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec)yloxy-1,2,4,5-tetrazine (4d).
Yield: 75%. mp: 86°C. IR (neat): υ (cm^{-1}) 2967 (C–H), 1478, 1448 (Tz), 1372 (C–S), 1146-1201 (C–F). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.85 (m, 2H, $O{-}CH_2(CH_2)_2S$), 4.67 (m, 2H, $C_8F_{17}{-}CH_2CH_2$), 2.75 (m, 4H, $C_8F_{17}{-}CH_2$, $O{-}CH_2CH_2CH_2{-}S$), 2.52 (m, 2H, $O(CH_2)_2CH_2{-}S$), 2.19 (m, 2H, $CH_3(CH_2)_2CH_2{-}S$), 1.57 (m, 2H, $CH_3CH_2CH_2CH_2{-}S$), 1.39 (m, 2H, $CH_2{-}CH_3$), 0.89 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.3; 165.8 ($C_{Tz}{-}O$), 100-120 (C_8F_{17}), 68.5 ($O{-}\underline{C}H_2(CH_2)_2S$), 61.7 ($C_8F_{17}{-}CH_2\underline{C}H_2$), 32 ($O{-}CH_2\underline{C}H_2CH_2{-}S$), 31.8 ($O(CH_2)_2\underline{C}H_2{-}S$), 30.8 (t, $^2J_{C\text{-}F}$ = 22 Hz, $C_8F_{17}{-}\underline{C}H_2$), 28.7 ($CH_3(CH_2)_2\underline{C}H_2{-}S$), 28.3 ($CH_3CH_2\underline{C}H_2CH_2{-}S$), 22.1 ($\underline{C}H_2{-}CH_3$), 13.7 ($CH_3$). ^{19}F NMR ($CDCl_3$): δ (ppm) -80.85 (m, 3F, CF_3), -113.47 (m, 2F, $CF_{2\alpha}$), -121.76 (m, 6F, $CF_{2\beta}CF_{2\gamma}CF_{2\delta}$), -122.75 (m, 2F, $CF_{2\varepsilon}$), -123.64 (m, 2F, $CF_{2\xi}$), -126.16 (m, 2F, $CF_{2\omega}$). Elem. Anal. Calcd for $C_{19}H_{19}F_{17}N_4O_2S$: C, 33.05; H, 2.77; N, 8.11; S, 4.64. Found: C, 33.15; H, 2.71; N, 8.36; S, 4.77.

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