Synthesis of dansyl-substituted cryptands containing triazacycloalkane moieties and their evaluation as fluorescent chemosensors

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Supporting information

Experimental part

General.

$^1$H and $^{13}$C NMR spectra were registered using “Bruker Avance-400” spectrometer (400 MHz for proton spectra and 100.6 MHz for carbon spectra) in CDCl$_3$ or DMSO-$d_6$ using residual chloroform or (CHD$_2$)CD$_3$SO signals as standards ($\delta_H$ 7.25 and $\delta_C$ 77.0 ppm, or $\delta_H$ 2.49 and $\delta_C$ 39.5 ppm, respectively). MALDI-TOF spectra of positive ions were obtained with “Bruker Daltonics Autoflex II” device using 1,8,9-trihydroxynathracene (dithranol) as matrix and poly(ethylene glycols) PEG-300, PEG-400, PEG-600 and PEG-1000 as internal standards for accurate mass measuring. UV-vis spectra were registered with “Agilent Cary 60” spectrophotometer, spectra of fluorescence were obtained using “Horiba Jobin Yvon Fluoromax 2” spectrofluorometer in acetonitrile (UHPLC grade). Preparative column chromatography was carried out using “Merck” silica gel (40-60 mesh). Commercially available oxadiamines 13a-d, 3- and 4-bromobenzyl bromides, 3-bromobenzyl chloride, 5-(dimethylamino)naphthalene-1-sulfonyl chloride (dansyl chloride) (3), sodium tert-butylate, phosphine ligands rac-BINAP and DavePhos were used without special purification. 1,4,7-Triazacyclononane (TACN) in the form of its trihydrochloride and 1,5,9-triazacyclododecane (TACD) were provided by the CheMatech Co (Dijon, France). Acetonitrile of UHPLC grade was used without additional purification, dioxane was successively distilled over NaOH and sodium. Chloroform was distilled over P$_2$O$_5$, dichloromethane was distilled over CaH$_2$, methanol was used freshly distilled. Pd(dba)$_2$ was synthesized according to method described in [1].
1,4,7-Triazacyclononane (1) [2]. A one-neck flask (10 ml) was charged with 1,4,7-triazacyclononane trihydrochloride (1190 mg, 5 mmol) in 2 ml water, sodium hydroxide (560 mg, 14 mmol) in 3 ml water was added in one portion. The mixture was stirred for 2 min, extracted with plenty of chloroform (5×50 ml), combined organic fractions were dried over anhydrous sodium sulfate, evaporated in vacuo, and TACN in the form of a free base was obtained as colorless hygroscopic crystals. Yield 478 mg (74%). 1H NMR (CDCl3) δ 2.02 (br. s, 3H, NH), 2.70 (s, 12H, CH2N). The spectrum is consistent with that given in literature.

General method for the synthesis of dansyl derivatives of triazacycloalkanes 4-7.

A one-neck flask equipped with a magnetic stirrer was charged with TACN (1) or TACD (2) (2-3 mmol) in acetonitrile (5 ml), potassium carbonate (10-15 mmol) and the solution of dansyl chloride (3) (1.4-2 mmol) in 65-100 ml acetonitrile was added slowly dropwise during ca 4 h. The residue was filtered off, washed with chloroform (in the case of TACN derivatives) or dichloromethane (in the case of TACD derivatives) (5 ml), the combined organic fractions were evaporated in vacuo and chromatographed on silica gel using a sequence of eluents: CHCl3, CHCl3 – MeOH 100:1 – 2:1, CHCl3 – MeOH – NH3aq 100:20:1 – 100:20:2 (for TACN derivatives) or CH2Cl2, CH2Cl2 – MeOH – MeOH 100:1 – 2:1 (for TACD derivatives).

5-(1,4,7-Triazacyclononan-1-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (4). Obtained from TACN (1) (387 mg, 3 mmol), dansyl chloride (3) (540 mg, 2 mmol) in the presence of potassium carbonate (2070 mg, 15 mmol) in 105 ml acetonitrile. Eluent CHCl3 – MeOH – NH3aq 100:20:1-100:20:2, yellow viscous oil. Yield 493 mg (68%). 1H NMR (CDCl3) δ 1.94 (br. s, 2H, NH), 2.82 (s, 6H, CH3), 2.84 (s, 4H, CH2NH), 3.02–3.06 (m, 4H, CH2NH), 3.33–3.37 (m, 4H, CH2NS), 7.13 (d, 3J= 7.6 Hz, 1H, H6(Nf)), 7.45 (dd, 3J= 8.5 Hz, 3J= 7.3 Hz, 1H, H3(Nf)), 7.50 (dd, 3J= 8.7 Hz, 3J= 7.6 Hz, 1H, H7(Nf)), 7.49 (dd, 3J= 7.3 Hz, 4J= 1.0 Hz, 1H, H2(Nf)), 8.43 (d, 3J= 8.7 Hz, 1H, H8(Nf)), 8.47 (d, 3J= 8.5 Hz, 1H, H4(Nf)). 13C NMR (CDCl3) δ 45.2 (2C, CH3), 49.2 (2C, CH2NH), 49.3 (2C, CH2NH), 53.7 (2C, CH2NS), 115.1 (1C, CH(Nf)), 119.6 (1C, CH(Nf)), 122.9 (1C, CH(Nf)), 127.9(1C, CH(Nf)), 128.0(1C, CH(Nf)), 129.9 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.2 (1C, C(Nf)), 135.5 (1C, C(Nf)), 151.5 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-300) m/z calcd. for C18H27N4O2S [M+H]+ 363.1849; found 363.1815.

5,5’-(1,4,7-Triazacyclononan-1,4-diylsulfonyl)bis(N,N-dimethylnaphthalen-1-amine) (6). Obtained as the second product in the synthesis of compound 4. Eluent CHCl3 – MeOH 15:1, yellow viscous oil. Yield 172 mg (29%). 1H NMR (CDCl3) δ 1.83 (br. s, 1H, NH), 2.85 (s, 12H,
$^{13}$C NMR (CDCl$_3$) $\delta$ 45.3 (4C, CH$_3$), 48.5 (2C, CH$_2$NH), 52.7 (2C, CH$_2$NS), 53.7 (2C, CH$_2$NS), 115.3 (2C, CH(Nf)), 119.4 (2C, CH(Nf)), 120.0 (2C, CH(Nf)), 128.2 (4C, CH(Nf)), 130.2 (4C, C(Nf), CH(Nf)), 130.3 (2C, C(Nf)), 134.2 (2C, C(Nf)), 151.7 (2C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C$_{30}$H$_{38}$N$_5$O$_4$S$_2$ [M+H]$^+$ 596.2360; found 596.2319.

$N,N$-Dimethyl-5-(1,4,7-triazabicyclo[5.2.1]dec-4-ylsulfonyl)naphthalene-1-amine ($4a$) is a by-product which can be obtained according to a scheme if using dichloromethane instead of chloroform in chromatographic isolation of compound 4:

\[
\begin{array}{c}
\text{4} \\
\text{CH$_2$Cl$_2$}$
\end{array}
\xrightarrow[K$_2$CO$_3$]{\text{NMe$_2$}}
\begin{array}{c}
\text{4a} \\
\text{CH$_2$Cl$_2$}
\end{array}
\]

Isolated with CH$_2$Cl$_2$ – MeOH – NH$_3$aq 100:20:1, yield widely depends on the overall chromatography time. $^{1}$H NMR (CDCl$_3$) $\delta$ 2.84 (s, 6H, CH$_3$), 3.06 (d, $^3$J = 15.2 Hz, 2H, CH$_2$N), 3.11–3.25 (m, 6H, CH$_2$N), 3.52 (ddd, $^2$J = 15.6 Hz, $^3$J = 11.4 Hz, $^3$J = 2.7 Hz, 2H, CH$_2$NS), 3.65 (d, $^2$J = 15.6 Hz, 2H, CH$_2$NS), 4.30 (d, $^2$J = 10.6 Hz, 1H, NCH$_2$N), 4.58 (d, $^2$J = 10.6 Hz, 1H, NCH$_2$N), 7.15 (d, $^3$J = 7.5 Hz, 1H, H6(Nf)), 7.47 (dd, $^3$J = 8.5 Hz, $^3$J = 7.5 Hz, 1H, H3(Nf)), 7.53 (dd, $^3$J = 8.6 Hz, $^3$J = 7.5 Hz, 1H, H7(Nf)), 7.96 (d, $^3$J = 7.5 Hz, 1H, H2(Nf)), 8.24 (d, $^3$J = 8.6 Hz, 1H, H8(Nf)), 8.51 (d, $^3$J = 8.5 Hz, 1H, H4(Nf)). $^{13}$C NMR (CDCl$_3$) $\delta$ 45.3 (2C, C$_3$H$_7$), 48.2 (2C, CH$_3$N), 48.9 (2C, CH$_2$N), 54.6 (2C, CH$_2$NS), 76.0 (1C, CH$_2$N$_2$), 115.4 (1C, CH(Nf)), 118.9 (1C, CH(Nf)), 118.9 (1C, CH(Nf)), 123.0 (1C, CH(Nf)), 128.4 (1C, CH(Nf)), 128.7 (1C, CH(Nf)), 129.9 (1C, C(Nf)), 130.2 (1C, C(Nf)), 130.6 (1C, CH(Nf)), 133.5 (1C, C(Nf)), 151.9 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-300) m/z calcd. for C$_{19}$H$_{27}$N$_4$O$_2$S [M+H]$^+$ 375.1855; found 375.1890.

3-(4-[[5-(Dimethylamino)-1-naphthyl]sulfonyl]-1,4,7-triazacyclononan-1-yl)propanenitrile ($4b$) is a by-product which can be obtained if using convenient acetonitrile containing ca 0.2 v/v % acrylonitrile according to a scheme:

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3
Eluent CH$_2$Cl$_2$ – MeOH 5:1, yield depends on the amount of acetonitrile applied. $^1$H NMR (CDCl$_3$) $\delta$ 2.64 (t, $^3$J = 6.2 Hz, 2H, CH$_2$N), 2.85 (s, 6H, CH$_3$), 2.93–2.97 (m, 2H, CH$_2$N), 2.99 (t, $^3$J = 6.2 Hz, 2H, NCH$_2$CCN), 3.02–3.07 (m, 2H, CH$_2$N), 3.38–3.46 (m, 4H, CH$_2$N), 3.52–3.56 (m, 2H, CH$_2$N), 3.80–3.85 (m, 2H, CH$_2$N), 7.16 (d, $^3$J = 7.5 Hz, 1H, H6(Nf)), 7.47 (dd, $^3$J = 7.5 Hz, 1H, H7(Nf)), 8.31 (d, $^3$J = 8.6 Hz, 1H, H8(Nf)), 8.52 (d, $^3$J = 8.5 Hz, 1H, H4(Nf)), NH proton was not unambiguously assigned. $^{13}$C NMR (CDCl$_3$) $\delta$ 16.6 (1C, CH$_2$CN), 45.3 (2C, CH$_3$), 46.1 (1C, CH$_2$N), 48.2 (1C, CH$_2$N), 50.2 (1C, CH$_2$N), 52.5 (1C, CH$_2$N), 53.0 (1C, CH$_2$N), 53.6 (1C, CH$_2$N), 55.7 (1C, CH$_2$N), 115.5 (1C, CH(Nf)), 119.0 (1C, CH(Nf)), 119.2 (1C, CN), 123.0 (1C, CH(Nf)), 128.3 (1C, CH(Nf)), 128.6 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.3 (1C, C(Nf)), 130.7 (1C, CH(Nf)), 133.0 (1C, C(Nf)), 151.9 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-400) m/z calcd. for C$_{21}$H$_{30}$N$_5$O$_2$S [M+H]$^+$ 416.2120; found 416.2089.

5-((1,5,9-Triazacyclododecan-1-yl)sulfonyl)-N,N-dimethylnaphthalene-1-amine (5). Obtained from TACD (2) (342 mg, 2 mmol) and dansyl chloride (3) (378 mg, 1.4 mmol) in the presence of potassium carbonate (1380 mg, 10 mmol) in 70 ml acetonitrile. Eluent CH$_2$Cl$_2$ – MeOH 5:1, yellow viscous oil. Yield 166 mg (28%). $^1$H NMR (CDCl$_3$) $\delta$ 1.83 (quintet, $^3$J = 5.2 Hz, 2H, CCH$_2$C), 2.06 (quintet, $^3$J = 5.7 Hz, 4H, CCH$_2$C), 2.84 (s, 6H, CH$_3$), 2.99 (t, $^3$J = 5.4 Hz, 4H, CH$_2$N), 3.07 (t, $^3$J = 5.2 Hz, 4H, CH$_2$N), 3.13 (t, $^3$J = 6.1 Hz, 4H, CH$_2$N), 7.14 (d, $^3$J = 7.5 Hz, 1H, H6(Nf)), 7.47–7.53 (m, 2H, H3, H7(Nf)), 8.07 (d, $^3$J = 7.5 Hz, 1H, H2(Nf)), 8.47 (d, $^3$J = 8.6 Hz, 1H, H8(Nf)), 8.55 (d, $^3$J = 8.5 Hz, 1H, H4(Nf)), two NH protons were not unambiguously assigned. $^{13}$C NMR (CDCl$_3$) $\delta$ 22.1 (1C, CCH$_2$C), 25.7 (2C, CCH$_2$C), 45.1 (2C, CH$_2$N), 45.3 (2C, CH$_3$), 49.1 (2C, CH$_2$N), 50.0 (2C, CH$_2$N), 115.3 (1C, CH(Nf)), 119.0 (1C, CH(Nf)), 123.0 (1C, CH(Nf)), 128.2 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.7 (1C, CH(Nf)), 131.0 (2C, CH(Nf), C(Nf)), 131.2 (1C, C(Nf)), 151.7 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-400) m/z calcd. for C$_{21}$H$_{33}$N$_4$O$_2$S [M+H]$^+$ 405.2324; found 405.2357.

5,5'-(1,5,9-Triazacyclododecane-1,5-diylsulfonyl)bis(N,N-dimethylnaphthalene-1-amine) (7). Obtained as the second product in the synthesis of compound 5. Eluent CH$_2$Cl$_2$ – MeOH 20:1, yellow crystalline powder, m.p. 158-160°C. Yield 288 mg (65%). $^1$H NMR (CDCl$_3$) $\delta$ 1.67
(quintet, $^3J = 5.5$ Hz, 4H, CCH$_2$C), 1.87 (quintet, $^3J = 6.9$ Hz, 4H, CCH$_2$C), 2.61 (t, $^3J = 5.4$ Hz, 2H, CH$_2$N), 2.87 (s, 12H, CH$_3$), 3.20 (t, $^3J = 6.9$ Hz, 4H, CH$_2$N), 3.27 (t, $^3J = 5.9$ Hz, 4H, CH$_2$N), 7.16 (d, $^3J = 7.5$ Hz, 2H, H6(Nf)), 7.47–7.53 (m, 4H, H3, H7(Nf)), 8.14 (dd, $^3J = 7.3$ Hz, $^4J = 0.8$ Hz, 2H, H2(Nf)), 8.35 (d, $^3J = 8.7$ Hz, 2H, H8(Nf)), 8.52 (d, $^3J = 8.5$ Hz, 2H, H4(Nf)), NH proton was not assigned. 13C NMR (CDCl$_3$) δ 23.8 (1C, CCH$_2$C), 27.8 (2C, CCH$_2$C), 42.9 (2C, CH$_2$N), 45.4 (6C, CH$_3$, CH$_2$N), 45.8 (2C, CH$_2$N), 115.1 (2C, CH(Nf)), 119.6 (2C, CH(Nf)), 123.1 (2C, CH(Nf)), 127.9 (2C, CH(Nf)), 130.0 (2C, C(Nf)), 130.1 (2C, CH(Nf)), 130.3 (4C, CH(Nf), C(Nf)), 134.0 (2C, C(Nf)), 135.6 (2C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C$_{33}$H$_{44}$N$_5$O$_4$S$_2$ [M+H]$^+$ 638.2835; found 638.2809.

3-(1,5,9-Triazacyclododecan-1-yl)propanenitrile (3a) is a by-product which can be obtained according to a scheme if using convenient acetonitrile containing ca 0.2 v/v % acrylonitrile:

\[ \text{NH} \quad \text{NH} \quad \text{NH} \quad \text{NH} \quad \text{CN} \]

\[ \text{3a} \]

\[ \text{5} \]

$^1$H NMR (CDCl$_3$) δ 1.59–1.69 (m, 6H, CCH$_2$C), 2.46 (t, $^3J = 6.8$ Hz, 2H, CH$_2$CN), 2.59 (t, $^3J = 5.6$ Hz, 4H, CH$_2$N), 2.69 (t, $^3J = 5.4$ Hz, 4H, CH$_2$N), 2.73–2.80 (m, 6H, 6H, CH$_2$N), two NH protons were not unambiguously assigned. 13C NMR (CDCl$_3$) δ 14.2 (1C, CH$_2$CN), 25.8 (1C, CCH$_2$C), 27.1 (2C, CCH$_2$C), 46.4 (2C, CH$_2$N), 47.3 (1C, CH$_2$N), 49.8 (2C, CH$_2$N), 52.1 (2C, CH$_2$N), quaternary carbon atom of CN group was not assigned due to its low intensity. MALDI-TOF m/z calcd. for C$_{12}$H$_{25}$N$_4$ [M+H]$^+$ 225.21; found 225.19.

3-(5-[[5-(Dimethylamino)-1-naphthyl]sulfonyl]-1,5,9-triazacyclododecan-1-yl)propanenitrile (5a) is a by-product which can be obtained if using convenient acetonitrile containing ca 0.2 v/v % acrylonitrile according to above-mentioned scheme. Eluent CH$_2$Cl$_2$ – MeOH 5:1. $^1$H NMR (CDCl$_3$) δ 1.83 (quintet, $^3J = 6.6$ Hz, 2H, CCH$_2$C), 1.89 (br. s, 2H, CCH$_2$C), 2.07 (br. s, 2H, CCH$_2$C), 2.55 (t, $^3J = 6.6$ Hz, 2H, CH$_2$CN), 2.57 (br. s, 2H, CH$_2$N), 2.71 (br. t, $^3J_{obs} = 5.0$ Hz, 2H, CH$_2$N), 2.76 (t, $^3J = 6.4$ Hz, 2H, CH$_2$N), 2.82 (s, 6H, CH$_3$), 3.15 (t, $^3J = 5.9$ Hz, 2H, CH$_2$N), 3.19–3.26 (m, 4H, CH$_2$N), 3.30 (t, $^3J = 6.1$ Hz, 2H, CH$_2$N), 7.12 (d, $^3J = 7.5$ Hz, 2H, CH$_2$N), 7.21–7.28 (m, 4H, CH$_2$N), 7.47–7.53 (m, 4H, CH$_2$N), 7.58–7.65 (m, 4H, CH$_2$N), 7.91–7.98 (m, 4H, CH$_2$N), 8.14 (dd, $^3J = 7.3$ Hz, $^4J = 0.8$ Hz, 2H, H2(Nf)), 8.35 (d, $^3J = 8.7$ Hz, 2H, H8(Nf)), 8.52 (d, $^3J = 8.5$ Hz, 2H, H4(Nf)), NH proton was not assigned. 13C NMR (CDCl$_3$) δ 23.8 (1C, CCH$_2$C), 27.8 (2C, CCH$_2$C), 42.9 (2C, CH$_2$N), 45.4 (6C, CH$_3$, CH$_2$N), 45.8 (2C, CH$_2$N), 115.1 (2C, CH(Nf)), 119.6 (2C, CH(Nf)), 123.1 (2C, CH(Nf)), 127.9 (2C, CH(Nf)), 130.0 (2C, C(Nf)), 130.1 (2C, CH(Nf)), 130.3 (4C, CH(Nf), C(Nf)), 134.0 (2C, C(Nf)), 135.6 (2C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C$_{33}$H$_{44}$N$_5$O$_4$S$_2$ [M+H]$^+$ 638.2835; found 638.2809.
Hz, 1H, H6(Nf)), 7.44–7.52 (m, 2H, H3,H7(Nf)), 8.03 (d, \(3J = 7.3\) Hz, 1H, H2(Nf)), 8.31 (d, \(3J = 8.6\) Hz, 1H, H8(Nf)), 8.50 (d, \(3J = 8.6\) Hz, 1H, H4(Nf)), NH proton was not unambiguously assigned. 13C NMR (CDCl3) \(\delta\) 14.8 (1C, CH2CN), 20.9 (1C, CCH2C), 23.5 (1C, CCH2C), 25.7 (1C, CCH2C), 42.8 (1C, CH2N), 44.8 (1C, CH2N), 45.2 (2C, CH3), 46.0 (1C, CH2N), 47.1 (1C, CH2N), 48.5 (1C, CH2N), 49.1 (1C, CH2N), 51.9 (1C, CH2N), 115.2 (1C, CH(Nf)), 119.0 (1C, CH(Nf)), 119.3 (1C, CN), 123.0 (1C, CH(Nf)), 128.2 (1C, CH(Nf)), 130.6 (1C, CH(Nf)), 130.9 (1C, C(Nf)), 130.9 (1C, CH(Nf)), 131.3 (1C, C(Nf)), 132.8 (1C, C(Nf)), 151.7 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-400) m/z calcd. for C24H36N5O2S [M+H]+ 458.2590; found 458.2556.

General method for the synthesis of dansyl and bromobenzyl derivatives of triazacycloalkanes 8-12.

A one-neck flask equipped with a magnetic stirrer was charged with a corresponding dansyl derivative of TACN (8, 9, 11) or TACD (10, 12) (0.31-1.12 mmol) which was solubilized in 0.3-0.5 ml chloroform (in the case of 8, 9) or dichloromethane, then acetonitrile (2-8 ml) was added to make a solution, followed by potassium carbonate (0.72-5.58 mmol), then appropriate bromobenzyl bromide (0.32-2.0 mmol) was added in one portion. The reaction mixture was stirred at ambient temperature for 24 h, then the residue was filtered off, washed with dichloromethane (5 ml), the combined organic fractions were evaporated in vacuo and, if necessary, chromatographed on silica gel using a sequence of eluents: CH2Cl2, CH2Cl2 – MeOH 100:1 – 2:1. In the case when chromatographic purification was unnecessary, the reaction mixture was dissolved in 5 ml dichloromethane, washed with water, dried over anhydrous sodium sulfate and evaporated in vacuo to dryness.

5-(4,7-Bis(3-bromobenzyl)-1,4,7-triazacyclononan-1-ylsulfonyl)-\(N,N\)-dimethylnaphthalen-1-amine (8). Obtained from compound 4 (405 mg, 1.12 mmol), 3-bromobenzyl bromide (500 mg, 2 mmol) in the presence of potassium carbonate (770 mg, 5.58 mmol) in 6 ml acetonitrile. Yellow glassy solid. Yield 577 mg (83%). 1H NMR (CDCl3) \(\delta\) 2.68 (br. s, 4H, CH2N), 2.84 (s, 6H, CH3), 3.04 (br. s, 4H, CH2N), 3.45 (br. s, 4H, CH2NS), 3.60 (s, 4H, PhCH2N), 7.13–7.18 (m, 3H, H6(Nf), H5(Ph)), 7.23 (br. s, 2H, H6(Ph)), 7.35 (d, \(3J = 7.8\) Hz, 2H, H4(Ph)), 7.44 (br. s, 2H, H2(Ph)), 7.47 (dd, \(3J = 8.5\) Hz, \(3J = 7.5\) Hz, 1H, H3(Nf)), 7.53 (dd, \(3J = 8.7\) Hz, \(3J = 7.7\) Hz, 1H, H7(Nf)), 8.01 (dd, \(3J = 7.5\) Hz, \(4J = 0.9\) Hz, 1H, H2(Nf)), 8.43 (d, \(3J = 8.7\) Hz, 1H, H8(Nf)), 8.49 (d, \(3J = 8.5\) Hz, 1H, H4(Nf)). 13C NMR (CDCl3) \(\delta\) 45.1 (2C, CH3), 50.2 (2C, CH2N) 54.9 (2C, CH2N), 55.1 (2C, CH2N), 61.4 (2C, NCH2Ph), 115.0 (1C, CH(Nf)), 119.5 (1C, CH(Nf)), 122.1 (2C, C3(Ph)), 122.9 (1C, CH(Nf)), 127.4 (2C, CH(Ph)), 127.8 (1C, CH(Nf)), 128.2 (1C,
CH(Nf)), 129.7 (2C, CH(Ph)), 129.8 (1C, CH(Nf)), 130.0 yu. (2CH(Ph), 2C(Nf)), 131.6 (2C, CH(Ph)), 135.0 (1C, C(Nf)), 142.0 (2C, C1(Ph)), 151.4 (1C, C(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C32H37Br2N4O2S [M+H]+ 699.1004; found 699.1034.

5-(4,7-Bis(4-bromobenzyl)-1,4,7-triazacyclononan-1-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (9). Obtained from compound 4 (340 mg, 0.94 mmol), 4-bromobenzyl bromide (350 mg, 1.5 mmol), in the presence of potassium carbonate (400 mg, 2.90 mmol) in 8 ml acetonitrile. Yellow glassy solid, yield 520 mg (99%). 1H NMR (CDCl3) δ 2.63 (br. s, 4H, CH2N), 2.84 (s, 6H, CH3), 3.02 (br. s, 4H, CH2N), 3.44 (br. s, 4H, CH2NS), 3.57 (s, 2H, PhCH2N), 7.15 (d, 3J= 8.3 Hz, 4H, H2, H2′(Ph)), 7.24 (d, 3J= 7.6 Hz, 1H, H6(Nf)), 7.39 (d, 3J= 8.3 Hz, 4H, H3, H3′(Ph)), 7.46 (dd, 3J= 8.5 Hz, 3J= 7.3 Hz, 1H, H3(Nf)), 8.40 (d, 3J= 8.6 Hz, 1H, H8(Nf)), 8.49 (d, 3J= 8.5 Hz, 1H, H4(Nf)). 13C NMR (CDCl3) δ 45.3 (2C, CH3), 50.2 (2C, CH2N), 55.2 (2C, CH2N), 55.4 (2C, CH2N), 61.7 (2C, PhCH2N), 115.2 (1C, CH(Nf)), 119.6 (1C, CH(Nf)), 120.7 (2C, C4(Ph)), 123.0 (1C, CH(Nf)), 128.0 (1C, CH(Nf)), 128.4 (1C, CH(Nf)), 130.9 (1C, C(Nf)), 130.2 (1C, C(Nf)), 130.7 (4CH(Ph), CH(Nf)), 131.3 (4C, CH(Ph)), 135.1 (1C, C(Nf)), 138.7 (2C, C1(Ph)), 151.6 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C32H37Br2N4O2S [M+H]+ 699.1004; found 699.1045.

5-((5,9-Bis(3-bromobenzyl)-1,5,9-triazacyclododecan-1-yl)sulfonyl)-N,N-dimethylnaphthalen-1-amine (10). Obtained from compound 5 (166 mg, 0.41 mmol), 3-bromobenzyl bromide (200 mg, 0.8 mmol), in the presence of potassium carbonate (500 mg, 3.62 mmol) in 4 ml acetonitrile. Eluent CH2Cl2 – MeOH 100:1, yellow glassy solid. Yield 113 mg (38%). 1H NMR (CDCl3) δ 1.57 (br. s, 4H, CCH2C), 2.22 (br. t, 3Jobs= 4.9 Hz, 4H, CH2N), 2.58 (br. s, 4H, CH2N), 2.86 (s, 6H, CH3), 3.57 (t, 3J= 7.6 Hz, 4H, CH2N), 3.39 (s, 4H, PhCH2N), 7.14–7.18 (m, 5H, H6(Nf), H(Ph)), 7.34–7.38 (m, 4H, H(Ph)), 7.46 (dd, 3J= 8.5 Hz, 3J= 7.3 Hz, 1H, H3(Nf)), 7.51 (dd, 3J= 8.7 Hz, 3J= 7.6 Hz, 1H, H7(Nf)), 8.13 (dd, 3J= 7.3 Hz, 4J= 0.9 Hz, 1H, H2(Nf)), 8.18 (d, 3J= 8.7 Hz, 1H, H7(Nf)), 8.48 (d, 3J= 8.5 Hz, 1H, H4(Nf)). 13C NMR (CDCl3) δ 23.1 (2C, CCH2C), 23.9 (1C, CCH2C), 41.3 (2C, CH2N), 45.4 (2C, CH3), 48.3 (2C, CH2N), 51.0 (2C, CH2N), 57.7 (2C, PhCH2N), 115.0 (1C, CH(Nf)), 119.5 (1C, CH(Nf)), 122.3 (2C, C3(Ph)), 123.1 (1C, CH(Nf)), 127.4 (2C, CH(Ph)), 127.8 (1C, CH(Nf)), 129.5 (1C, CH(Nf)), 129.8 (2C, CH(Ph)), 129.9 (br.s, CH(Nf), 2CH(Ph), 2C(Nf)), 131.8 (2C, CH(Ph)), 135.7 (1C, C(Nf)), 141.8 (2C, C1(Ph)), 151.6 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C32H37Br2N4O2S [M+H]+ 741.1473; found 741.1449.
5-((5-(3-Bromobenzyl)-1,5,9-triazacyclododecan-1-yl)sulfonyl)-N,N-dimethylnaphthalen-1-amine (10a). Obtained as the second product in the synthesis of compound 10 according to a scheme:

![Reaction Scheme](image)

Eluent CH2Cl2 – MeOH 10:1, yellow viscous oil. Yield 54 mg (23%). 1H NMR (CDCl3) δ 1.84–1.94 (m, 4H, CCH2C), 2.16 (br. s, 2H, CCH2C), 2.61 (br. t, 3Jobs= 4.9 Hz, 4H, CH2N), 2.86 (s, 6H, CH3), 3.03 (br. t, 3Jobs= 5.1 Hz, 2H, CH2N), 3.15–3.25 (m, 4H, CH2N), 3.30 (br. t, 3J= 5.4 Hz, 2H, CH2N), 3.57 (s, 2H, PhCH2N), 7.17 (d, 3J= 7.6 Hz, 1H, H6(Nf)), 7.23–7.31 (m, 2H, H(Ph)), 7.36 (br. s, 1H, H2(Ph)), 7.38 (dd, 3J= 7.7 Hz, 4J= 1.7 Hz, 1H, H4(Ph)), 7.49–7.55 (m, 2H, H3, H7(Nf)), 8.06 (d, 3J= 7.1 Hz, 1H, H2(Nf)), 8.37 (d, 3J= 8.7 Hz, 1H, H8(Nf)), 8.55 (d, 3J= 8.5 Hz, 1H, H4(Nf)), NH proton was not assigned. 13C NMR (CDCl3) δ 26.3 (2C, CCH2C), 26.5 (1C, CCH2C), 43.6 (1C, CH2N), 45.4 (2C, CH3), 46.2 (1C, CH2N), 47.3 (1C, CH2N), 48.2 (1C, CH2N), 49.7 (1C, CH2N), 52.8 (1C, CH2N), 57.3 (1C, PhCH2N), 115.3 (1C, CH(Nf)), 119.1 (1C, CH(Nf)), 122.5 (1C, C3(Ph)), 123.1 (1C, CH(Nf)), 128.3 (2C, CH(Ph), CH(Nf)), 129.9 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.5 (1C, C(Nf)), 130.8 (3C, 2CH(Ph), CH(Nf)), 132.5 (1C,
CH(Ph)), 138.9 (1C, C(Nf)), 141.5 (1C, C1(Ph)), 151.8 (1C, N(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C_{28}H_{38}BrN_{4}O_{2}S [M+H]^+ 573.1899; found 573.1934.

5,5′-(7-(3-Bromobenzyl)-1,4,7-triazacyclononan-1,4-disulfonyl)bis(N,N-dimethylnaphthalen-1-amine) (11). Obtained from compound 6 (259 mg, 0.434 mmol), 3-bromobenzyl bromide (108 mg, 0.432 mmol), in the presence of potassium carbonate (300 mg, 2.17 mmol) in 2 ml acetonitrile. Yellow glassy solid, yield 305 mg (92%). ¹H NMR (CDCl₃) δ 2.82 (s, 12H, CH₃), 3.01 (br. s, 4H, CH₂N), 3.41 (br. s, 4H, CH₂NS), 3.66 (s, 4H, CH₂NS), 3.69 (s, 2H, NCH₂Ph), 7.14 (d, 3J = 7.7 Hz, 2H, H₆(Nf)), 7.12–7.17 (m, 1H, H₅(Ph)), 7.33 (d, 3J = 8.0 Hz, 1H, H₆(Ph)), 7.43 (d, 3J = 7.8 Hz, 1H, H₄(Ph)), 7.46 (dd, 3J = 8.5 Hz, 3J = 7.2 Hz, 2H, H₃(Nf)), 7.51 (dd, 3J = 8.6 Hz, 3J = 7.7 Hz, 2H, H₇(Nf)), 7.53 (br. s, 1H, H₂(Ph)), 7.93 (d, 3J = 7.2 Hz, 2H, H₂(Nf)), 8.40 (d, 3J = 8.6 Hz, 2H, H₈(Nf)), 8.49 (d, 3J = 8.5 Hz, 2H, H₄(Nf)). ¹³C NMR (CDCl₃) δ 45.1 (4C, CH₃), 51.4 (2C, CH₂N), 52.1 (2C, CH₂N), 53.8 (2C, CH₂N), 59.9 (1C, PhCH₂N), 115.1 (2C, CH(Nf)), 119.3 (2C, CH(Nf)), 122.1 (1C, C₃(Ph)), 122.9 (2C, CH(Nf)), 127.6 (1C, CH(Ph)), 127.9 (2C, CH(Nf)), 128.0 (2C, CH(Nf)), 129.8 (1C, CH(Ph)), 129.9 (br. s, 2CH(Nf), 2C(Nf), CH(Ph)), 130.0 (2C, C(Nf)), 131.7 (1C, CH(Ph)), 134.2 (2C, C(Nf)), 141.7 (1C, C₁(Ph)), 151.5 (2C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C₃₇H₄₃BrN₅O₄S₂ [M+H]^+ 764.1940; found 764.1998.

5,5′-(9-(3-Bromobenzyl)-1,5,9-triazacyclododecane-1,5-disulfonyl)bis(N,N-dimethylnaphthalen-1-amine) (12). Obtained from compound 7 (200 mg, 0.31 mmol), 3-bromobenzyl bromide (80 mg, 0.32 mmol), in the presence of potassium carbonate (100 mg, 0.72 mmol) in 2 ml acetonitrile. Yellow glassy solid, yield 231 mg (93%). ¹H NMR (CDCl₃) δ 1.72 (quintet, 3J = 6.1 Hz, 4H, CCH₂C), 1.90 (quintet, 3J = 6.7 Hz, 2H, CCH₂C), 2.38 (t, 3J = 5.9 Hz, 4H, CH₂N), 2.86 (s, 12H, CH₃), 3.24 (t, 3J = 6.4 Hz, 4H, CH₂N), 3.35 (t, 3J = 6.8 Hz, 4H, CH₂N), 3.37 (s, 2H, PhCH₂N), 7.10–7.14 (m, 2H, H(Ph)), 7.15 (d, 3J = 7.5 Hz, 2H, H₆(Nf)), 7.32–7.35 (m, 2H, H(Ph)), 7.47–7.53 (m, 4H, H₃, H₇(Nf)), 8.11 (d, 3J = 7.3 Hz, 2H, H₂(Nf)), 8.32 (d, 3J = 8.6 Hz, 2H, H₈(Nf)), 8.52 (d, 3J = 8.5 Hz, 2H, H₄(Nf)). ¹³C NMR (CDCl₃) δ 24.6 (1C, CCH₂C), 24.8 (2C, CCH₂C), 43.6 (2C, CH₂N), 45.0 (2C, CH₂N), 45.3 (4C, CH₃), 49.5 (2C, CH₂N), 58.0 (1C, PhCH₂N), 115.1 (2C, CH(Nf)), 119.4 (2C, CH(Nf)), 122.3 (1C, C₃(Ph)), 123.0 (2C, CH(Nf)), 127.3 (1C, CH(Ph)), 127.9 (2C, CH(Nf)), 129.7 (2C, CH(Nf)), 129.8 (1C, CH(Ph)), 129.9 (2C, C(Nf)), 130.0 (1C, CH(Ph)), 130.1 (2C, C(Nf)), 130.3 (2C, CH(Nf)), 131.8 (1C, CH(Ph)), 134.3 (2C, C(Nf)), 141.4 (1C, C₁(Ph)), 151.6 (2C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C₄₀H₄₉BrN₅O₄S₂ [M+H]^+ 806.2409; found 806.2369.
Typical experimental procedure for the synthesis of the cryptands 14-16. A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with corresponding triazacycloalkane derivative **8-10** (0.15-0.29 mmol), Pd(dba)$_2$ (16 mol%), DavePhos (18 mol%), absolute dioxane (10-15 ml). The mixture was stirred for 2-3 min, then corresponding oxadiamine (0.15-0.29 mmol) was added followed by tBuONa (0.45-0.9 mmol). The reaction mixture was stirred at reflux for 24 h, cooled down to ambient temperature, the residue was filtered off, washed with dichloromethane (5 ml), combined organic fractions were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents CH$_2$Cl$_2$, CH$_2$Cl$_2$–MeOH 100:1–2:1, CH$_2$Cl$_2$–MeOH–NH$_3$aq100:20:1–10:4:1.

**5-(10,13,16-Trioxa-6,20-diaza-3(1,4)-triazacyclononane-1,5(1,3)-dibenzenacycloicosaphan-37-ylsulfonyl)-N,N-dimethylnaphthalenyl-1-amine (14a).** Obtained from compound 8 (140 mg, 0.2 mmol), trioxadiamine 13a (44 mg, 0.2 mmol), in the presence of Pd(dba)$_2$ (18 mg, (0.032 mmol), DavePhos (14 mg, 0.036 mmol), tBuONa (58 mg, 0.6 mmol) in 10 ml dioxane. Eluent CH$_2$Cl$_2$–MeOH 3:1, yield 37 mg (24%), yellow glassy solid. UV-vis (CH$_3$CN): $\lambda_{\text{max}}$ 305 nm (log $\varepsilon$ 3.76), 340 nm (log $\varepsilon$ 3.48). $^1$H NMR (CDCl$_3$, 298 K) $\delta$ 1.85 (br. quintet, $^3J_{\text{obs}}= 5.7$ Hz, 4H, CH$_2$CH$_2$CH$_2$), 2.86 (br. s, 4H, CH$_2$N), 2.87 (s, 6H, CH$_3$) 3.08–4.00 (br. m, 12H, CH$_2$N, PhCH$_2$N), 3.24 (br. t, $^3J_{\text{obs}}= 4.8$ Hz, 4H CH$_2$NPh), 3.55–3.60 (br. m, 8H, CH$_2$O), 3.61–3.66 (br. m, 4H, CH$_2$O), 6.58 (br. s, 2H, H(Ph)), 6.60 (br. d, $^3J_{\text{obs}}= 6.9$ Hz, 2H, H(Ph)), 6.84 (br. s, 2H, H2(Ph)), 7.10 (t, $^3J= 7.7$ Hz, 2H, H5(Ph)), 7.15 (d, $^3J= 7.6$ Hz, 1H, H6(Nf)), 7.49 (t, $^3J_{\text{obs}}= 7.8$ Hz, 1H, H3(Nf)), 7.53 (t, $^3J_{\text{obs}}= 8.2$ Hz, 1H, H7(Nf)), 7.98 (br. s, 1H, H2(Nf)), 8.34 (d, $^3J= 7.6$ Hz, 1H, H8(Nf)), 8.54 (d, $^3J= 8.2$ Hz, 1H, H4(Nf)), 2NH protons were not unambiguously assigned. $^{13}$C NMR (CDCl$_3$, 298 K ) $\delta$ 28.7 (2C, CCH$_2$C), 41.4 (2C , CH$_2$NPh), 45.3 (2C , CH$_3$, 47.0–57.0 (br. m, 6C, CH$_2$N), 61.7 (br. s, 2C, $\Delta\nu_{1/2}= 100$ Hz, PhCH$_2$N), 69.4 (2C, CH$_2$O), 70.1 (2C, CH$_2$O), 70.5 (2C, CH$_2$O), 112.7 (br. s, 2C, $\Delta\nu_{1/2}= 60$ Hz, CH(Ph)), 114.3 (br. s, 2C, $\Delta\nu_{1/2}= 30$ Hz, (CH(Ph)), 115.4 (1C, CH(Nf)), 118.1 (1C, CH(Nf)), 119.0 (br. s, 2C, $\Delta\nu_{1/2}= 30$ Hz, (CH(Ph)), 123.1 (1C, (CH(Nf)), 128.2–131.0 (br. m, 3C(Ph), 2C5(Ph), 2C(Nf)), 134.4 (1C, C(Nf)), 137.5 (2C, C1(Ph)), 149.2 (br. s, 2C, $\Delta\nu_{1/2}= 20$ Hz, C3(Ph)), 151.9 (1C, NC(Nf)). $^1$H NMR (DMSO-$d_6$, 363 K) $\delta$ 1.77 (quintet, $^3J= 6.2$ Hz, 4H, CCH$_2$C), 2.75–3.25 (br. m, 12H, CH$_2$N), 2.86 (s, 6H, CH$_3$), 3.12 (t, $^3J= 6.5$ Hz, 4H, CH$_2$NPh), 3.46–3.56 (m, 12H, CH$_2$O), 3.69 (br. s, 4H, PhCH$_2$N), 6.52 (br. d, $^3J_{\text{obs}}= 7.0$ Hz, 2H, H(Ph)), 6.54 (br. s, 4H, H(Ph)), 7.03 (br. t, $^3J_{\text{obs}}= 6.4$ Hz, 2H, H5(Ph)), 7.28 (d, $^3J= 7.6$ Hz, 1H, H6(Nf)), 7.60 (t, $^3J_{\text{obs}}= 8.3$ Hz, 1H, H3(Nf)), 7.62 (t, $^3J= 7.6$ Hz, 1H, H7(Nf)), 8.06 (d, $^3J= 7.3$ Hz, 1H, H2(Nf)), 8.35 (d, $^3J= 8.6$ Hz, 1H, H8(Nf)), 8.53 (br. d, $^3J= 8.3$ Hz, 1H, H4(Nf)), two NH protons were not unambiguously assigned. $^{13}$C NMR (DMSO-$d_6$, 363 K ) $\delta$ 28.7 (2C, CCH$_2$C), 44.3 (2C, CH$_3$), 48.0 (br. s, 2C,
\( \Delta \nu_{1/2} = 60 \text{ Hz}, \text{CH}_2\text{N} \), 53.5 (br. s, 2C, \( \Delta \nu_{1/2} = 50 \text{ Hz}, \text{PhCH}_2\text{N} \), 67.9 (2C, \text{CH}_2\text{O}), 69.2 (2C, \text{CH}_2\text{O}), 69.5 (2C, \text{CH}_2\text{O}), 111.9 (2C, \text{CH(Ph)}), 112.1 (2C, \text{CH(Ph)}), 112.1 (2C, \text{CH(Ph)}), 114.9 (1C, \text{CH(Nf)}), 116.4 (2C, \text{CH(Ph)}), 118.3 (1C, \text{CH(Nf)}), 122.8 (1C, \text{CH(Nf)}), 127.5 (1C, \text{CH(Nf)}), 127.8 (1C, \text{CH(Nf)}), 128.2 (1C, \text{CH(Nf)}), 129.2 (2C, \text{C5(Ph)}), 148.7 (2C, \text{C3(Ph)}), 151.2 (1C, \text{NC(Nf)}) four quaternary carbon atoms were not assigned due to line broadening: C(1Ph) and three quaternary carbon atoms in naphthalene; the following signals overlap with CD$_3$ multiplet from the solvent: CH$_2$N and CH$_2$NHPh (in the trioxadiamine chain). HRMS MALDI-TOF (PEG-600) m/z calc'd. for C$_{42}$H$_{59}$N$_6$O$_5$S $[M+H]^+$ 759.4268; found 759.4223.

5-(9,12,15-Trioxa-6,18-diaza-3(1,4)-triazacyclononan-1,5(1,3)-dibenzenocyclooctadecaphan-37-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (14b). Obtained from compound 8 (200 mg, 0.285 mmol), trioxadimaine 13b (55 mg, 0.285 mmol), in the presence of Pd (dba)$_2$ (26 mg, 0.046 mmol), DavePhos (20 mg, 0.051 mmol), tBuONa (82 mg, 0.86 mmol) in 15 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH 2:1, yield 42 mg (20%), yellow glassy solid. UV-vis (CH$_3$CN): \( \lambda_{\text{max}} 305 \text{ nm (log } \varepsilon 3.73) \), 340 nm (log \( \varepsilon 3.43) \). $^1$H NMR (CDCl$_3$) \( \delta \) 2.86 (s, 6H, CH$_3$), 3.31 (br. s, 4H, CH$_2$NPh), 3.05–4.20 (br. m, 16H, CH$_2$N, PhCH$_2$N), 3.64 (s, 8H, CH$_2$O), 3.70 (br. t, \( ^3J_{obs} = 4.2 \text{ Hz}, 4 \text{H, CH}_2\text{O}) , 4.73 (br. s, 2H, NH), 6.56 (br. d, \( ^3J_{obs} = 7.7 \text{ Hz}, 2 \text{H, CH(Ph)}), 6.61 (br. d, \( ^3J_{obs} = 5.9 \text{ Hz}, 2 \text{H, CH(Ph)}), 6.85 (br. s, 2H, H2(Ph)), 7.09 (t, \( ^3J_{obs} = 7.7 \text{ Hz, 2H, H5(Ph)}), 7.17 (d, \( ^3J_{obs} = 7.5 \text{ Hz, 1H, H6(Nf)}), 7.48 (t, \( ^3J_{obs} = 7.7 \text{ Hz, 1H, H3(Nf)}), 7.53 (t, \( ^3J_{obs} = 8.1 \text{ Hz, 1H, H7(Nf)}), 7.96 (br. s, 1H, H2(Nf)), 8.33 (br. d, \( ^3J_{obs} = 4.6 \text{ Hz, 1H, H8(Nf)}), 8.53 (br. d, \( ^3J_{obs} = 8.2 \text{ Hz, 1H, H4(Nf)}). ^{13} \text{C NMR (CDCl}_3) \delta 43.6 (2 \text{C, CH}_2\text{NPh}, 45.3 (2 \text{C, CH}_3), 50.6 (br. s, 4 \text{C, CH}_2\text{N}), 55.3 (br. s, 2 \text{C, CH}_2\text{N}), 61.6 (br. s, 2 \text{C, } \Delta \nu_{1/2} = 50 \text{ Hz, PhCH}_2\text{N}), 69.4 (2 \text{C, CH}_2\text{O}), 70.3 (2 \text{C, CH}_2\text{O}), 70.7 (2 \text{C, CH}_2\text{O}), 112.9 (br. s, 2 \text{C, } \Delta \nu_{1/2} = 40 \text{ Hz, CH(Ph)}), 114.9 (br. s, 2 \text{C, } \Delta \nu_{1/2} = 35 \text{ Hz, CH(Ph)}), 115.4 (1 \text{C, CH(Nf)}), 118.5 (1 \text{C, CH(Nf)}), 119.1 (br. s, 2 \text{C, } \Delta \nu_{1/2} = 30 \text{ Hz, CH(Ph)}), 123.0 (1 \text{C, CH(Nf)}), 128.1–130.8 (br. m, 2 \text{C5(Ph), 3CH(Nf), 2CNf}), 133.5 (1 \text{C, C(Nf)}), 143.5 (2 \text{C, C1(Ph)}), 149.0 (br. s, 2 \text{C, } \Delta \nu_{1/2} = 30 \text{ Hz, C3(Ph)}), 151.9 (1 \text{C, NC(Nf)}). HRMS MALDI-TOF (PEG-600) m/z calc'd. for C$_{40}$H$_{55}$N$_6$O$_5$S $[M+H]^+$ 731.3955; found 731.3988.

5-(10,15-Dioxa-6,19-diaza-3(1,4)-triazacyclononan-1,5(1,3)-dibenzenocyclononadecaphan-37-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (14c). Obtained from compound 8 (202 mg, 0.288 mmol), dioxadiamine 13c (59 mg, 0.288 mmol), in the presence of Pd(dba)$_2$ (27 mg, 0.046 mmol), DavePhos (20 mg, 0.052 mmol), tBuONa (83 mg, 0.86 mmol), in 15 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH 10:1 – 5:1, yield 48 mg (22%), yellow glassy solid. UV-vis (CH$_3$CN): \( \lambda_{\text{max}} 340 \)
nm (log ε 3.48). $^1$H NMR (CDCl$_3$) δ 1.64 (br. s, 4H, CCH$_2$CH$_2$C), 1.84 (br. quintet, $^3$J$_{obs}$ = 5.5 Hz, 4H, CCH$_2$NPh), 3.42 (br. s, 4H, CH$_2$O), 3.52 (br. t, $^3$J$_{obs}$ = 3.9 Hz, 4H, CH$_2$O), 6.52 (br. s, 2H, H(Ph)), 6.58 (d, $^3$J$_{obs}$ = 7.5 Hz, 2H, H(Ph)), 6.84 (br. s, 2H, H(Ph)), 7.09 (t, $^3$J$_{obs}$ = 7.6 Hz, 2H, H(Ph)). 7.15 (d, $^3$J$_{obs}$ = 7.3 Hz, 1H, H(Ph)), 7.48 (t, $^3$J$_{obs}$ = 7.7 Hz, 1H, H(Ph)), 7.53 (t, $^3$J$_{obs}$ = 8.2 Hz, 1H, H(Ph)), 7.97 (br. s, 2H, H(Ph)), 8.36 (br. d, $^3$J$_{obs}$ = 6.8 Hz, 1H, H(Ph)), 8.52 (br. d, $^3$J$_{obs}$ = 7.7 Hz, 1H, H(Ph)).

Two NH protons were not unambiguously assigned. $^{13}$C NMR (CDCl$_3$) δ 26.5 (2C, CCH$_2$CH$_2$C), 29.1 (2C, CCH$_2$C), 41.9 (2C, CH$_2$NPh), 45.3 (2C, CH$_3$), 50.4 (br. s, 2C, $\Delta$ν$_{1/2}$ = 120 Hz, CH$_3$N), 54.6 (br. s, 4C, $\Delta$ν$_{1/2}$ = 200 Hz, CH$_2$N), 61.7 (br. s, 2C, $\Delta$ν$_{1/2}$ = 130 Hz, PhCH$_2$N), 69.2 (2C, CH$_2$O), 70.7 (2C, CH$_2$O), 112.4 (br. s, 2C, $\Delta$ν$_{1/2}$ = 70 Hz, CH(Ph)), 114.2 (br. s, 2C, $\Delta$ν$_{1/2}$ = 50 Hz, CH(Ph)), 115.4 (1C, CH(Ph)), 118.1 (1C, CH(Ph)), 119.2 (br. s, 2C, $\Delta$ν$_{1/2}$ = 60 Hz, CH(Ph)), 123.0 (1C, CH(Ph)), 127.9–131.0 (br. m, 3CH(Ph)), 134.6 (1C, C(Ph)), 141.2 (2C, C(Ph)), 149.2 (br. s, 2C, $\Delta$ν$_{1/2}$ = 40 Hz, C(Ph)), 151.9 (1C, NC(Ph)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C$_{42}$H$_{59}$N$_6$O$_4$S [M+H]$^+$ 743.4319; found 743.4306.

5-(9,12-Dioxa-6,15-diaza-3(1,4)-diazacyclononan-1,5(1,3)-dibenzenocyclopentadecaphan-37-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (14d). Obtained from compound 8 (140 mg, 0.2 mmol), dioxadiamine 13d (30 mg, 0.2 mmol), in the presence of Pd(dba)$_2$ (9 mg, 0.016 mmol), BINAP (11 mg, 0.018 mmol), tBuONa (58 mg, 0.6 mmol), in 10 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH 5:1, yield 15 mg (11%), yellow glassy solid. UV-vis (CH$_3$CN): $\lambda_{max}$ 305 nm (log ε 3.71), 340 nm (log ε 3.48). $^1$H NMR (CDCl$_3$) δ 2.86 (s, 6H, CH$_3$N), 3.10–4.15 (br. m, 16H, CH$_2$N, PhCH$_2$N), 3.31 (t, $^3$J$_{obs}$ = 4.7 Hz, 4H, CH$_2$NPh), 3.67 (s, 4H, CH$_2$O), 3.74 (s, 4H, CH$_2$O), 6.58 (d, $^3$J$_{obs}$ = 7.7 Hz, 2H, H(Ph)), 6.70 (br. s, 2H, H(Ph)), 6.87 (br. s, 2H, H(Ph)), 7.14 (t, $^3$J$_{obs}$ = 7.8 Hz, 2H, H(Ph)), 7.16 (d, $^3$J$_{obs}$ = 7.7 Hz, 1H, H(Ph)), 7.48 (dd, $^3$J$_{obs}$ = 8.5 Hz, $^3$J$_{obs}$ = 7.5 Hz, 1H, H(Ph)), 7.52 (dd, $^3$J$_{obs}$ = 8.8 Hz, $^3$J$_{obs}$ = 7.7 Hz, 1H, H(Ph)), 7.98 (br. d, $^3$J$_{obs}$ = 6.2 Hz, 1H, H(Ph)), 8.28 (d, $^3$J$_{obs}$ = 8.8 Hz, 1H, H(Ph)), 8.53 (d, $^3$J$_{obs}$ = 8.5 Hz, 1H, H(Ph)), two NH protons were not unambiguously assigned. $^{13}$C NMR (CDCl$_3$) δ 43.7 (2C, CH$_2$NPh), 45.3 (2C, CH$_3$), 51.8 (br. s, 6C, $\Delta$ν$_{1/2}$ = 290 Hz, CH$_3$N), 60.8 (br. s, 2C, $\Delta$ν$_{1/2}$ = 150 Hz, PhCH$_2$N), 69.2 (2C, CH$_2$O), 70.0 (2C, CH$_2$O), 112.6 (br. s, 2C, $\Delta$ν$_{1/2}$ = 30 Hz, CH(Ph)), 115.5 (1C, CH(Ph)), 116.4 (br. s, 2C, $\Delta$ν$_{1/2}$ = 20 Hz, CH(Ph)), 118.9 (1C, CH(Ph)), 119.2 (2C, CH(Ph)), 123.1 (1C, CH(Ph)), 128.6 (1C, CH(Ph)), 129.9 (1C, CH(Ph)), 130.3 (2C, CH(Ph)), 130.8 (1C, CH(Ph)), 132.0 (1C, C(Ph)), 133.3 1C, C(Ph)), 148.9 (br. s, 2C, $\Delta$ν$_{1/2}$ = 30 Hz, C3(Ph)), 151.9 (1C, NC(Ph)). two quaternary carbon atoms: C1(Ph) and one of the naphthalene moiety were not
unambiguously assigned. HRMS MALDI-TOF (PEG-600) m/z calcd. for C₃₈H₅₁N₆O₄S [M+H]+ 687.3692; found 687.3751.

5-(10,13,16-Trioxa-6,20-di­aza-3(1,4)-triaza­cyclononan-1,5(1,4)-di­benzenocycloicosaphan-3²-ylsulfon­yl)-N,N-di­methylnaphtha­len-1-amine (15a). Obtained from compound 9 (125 mg, 0.178 mmol), trioxa­di­amine 13a (39 mg, 0.178 mmol), in the presence of Pd(dba)₂ (16 mg, 0.028 mmol), DavePhos (13 mg, 0.032 mmol), BuONa (51 mg, 0.53 mmol), in 10 ml dioxane. Eluent CH₂Cl₂ – MeOH 2:1, yield 21 mg (15%), yellow glassy solid. UV-vis (CH₃CN): λₘₐₓ 305 nm (log ε 3.56), 340 nm (log ε 3.48). ¹H NMR (CDCl₃) δ 1.88 (br. quintet, 3 Jₖₑₜ = 5.7 Hz, 4H, CCH₂C), 2.88 (s, 6H, CH₃), 3.10–4.00 (br. m, 16 H, CH₂N, PhCH₂N), 3.26 (br. t, 3 Jₖₑₜ = 5.8 Hz, 4H, CH₂NPh), 3.58–3.63 (m, 8H, CH₂O), 3.67–3.71 (m, 4H, CH₂O), 4.52 (br. s, 2H, NH), 6.55 (d, 3 Jₖₑₜ = 8.1 Hz, 4H, H2, H2’(Ph)), 7.03 (br. s, 4H, H3, H3’(Ph)), 7.19 (d, 3 Jₖₑₜ = 7.3 Hz, 1H, H6(Nf)), 7.52 (t, 3 Jₖₑₜ = 8.0 Hz, 1H, H3(Nf)), 7.55 (t, 3 Jₖₑₜ = 7.9 Hz, 1H, H7(Nf)), 8.04 (br. s, 1H, H2(Nf)), 8.31 (d, 3 Jₖₑₜ = 8.8 Hz, 1H, H8(Nf)), 8.56 (d, 3 Jₖₑₜ = 8.6 Hz, 1H, H4(Nf)). ¹³C NMR (CDCl₃) δ 28.7 (2C, C CH₂C), 42.1 (CH₂NHPh), 45.4 (2C, CH₃), 47.9–53.5 (br. m, 6C, CH₂N), 60.6 (br. s, 2C, Δ ν₁/₂= 50 Hz, PhCH₂N), 70.1 (2C, CH₂O), 70.2 (2C, CH₂O), 70.7 (2C, CH₂O), 912.9 (4C, CH(Ph)), 115.5 (1C, CH(Nf)), 118.7 (1C, CH(Nf)), 123.1 (1C, CH(Nf)), 128.6 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.3 (2C, C1(Ph)), 130.7 (1C, C(Nf)), 131.1 (1C, C(Nf)), 131.6 (6C, 4CH(Ph), 2CH(Nf)), 149.0 (2C, C4(Ph)), 152.0 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C₄₂H₅₉N₆O₅S [M+H]+ 759.4268; found 759.4223.

5-(9,12,15-Trioxa-6,18-di­aza-3(1,4)-triaza­cyclononan-1,5(1,4)-di­benzenocyclooctadecaphan-3²-ylsulfon­yl)-N,N-di­methylnaphtha­len-1-amine (15b). Obtained from compound 9 (119 mg, 0.17 mmol), trioxa­di­amine 13b (33 mg, 0.17 mmol), in the presence of Pd(dba)₂ (16 mg, 0.0272 mmol), DavePhos (12 mg, 0.0306 mmol), BuONa (24 mg, 0.254 mmol), in 10 ml dioxane. Eluent CH₂Cl₂ – MeOH 5:1, yield 11 mg (9%), yellow glassy solid. ¹H NMR (CDCl₃) δ 2.88 (s, 6H, CH₃), 3.15 (br. s, 4H, CH₂N), 3.31 (br. q, 3 Jₖₑₜ = 4.8 Hz, 4H, CH₂NPh) 3.45–3.85 (m, 20H, CH₂O), 3.98 (br. s, 4H, PhCH₂N), 6.47 (d, 3 Jₖₑₜ = 8.2 Hz, 4H, H2, H2’(Ph)), 6.96 (br. s, 4H, H3, H3’(Ph)), 7.19 (d, 3 Jₖₑₜ = 7.7 Hz, 1H, H6(Nf)), 7.52 (t, 3 Jₖₑₜ = 7.8 Hz, 1H, H3(Nf)), 7.55 (t, 3 Jₖₑₜ = 8.0 Hz, 1H, H7(Nf)), 7.89 (br. s, 1H, H2(Nf)), 8.29 (d, 3 Jₖₑₜ = 8.8 Hz, 1H, H8(Nf)), 8.57 (d, 3 Jₖₑₜ = 8.7 Hz, 1H, H4(Nf)), two NH protons were not unambiguously assigned. ¹³C NMR (CDCl₃) δ 43.5 (2C, CH₂NPh), 45.3 (2C, CH₃), 46.5–51.0 (br. m, 6C, CH₂N), 61.6 (br. s, 2C, PhCH₂N), 69.0 (2C, CH₂O), 70.2 (2C, CH₂O), 70.6 (2C, CH₂O), 113.4 (4C, C2, C2’(Ph)), 115.5 (1C, CH(Nf)), 118.8 (1C, CH(Nf)), 123.1 (1C, CH(Nf)), 128.6 (4C, C3, C3’(Ph)), 130.0 (1C, CH(Nf)), 130.3 (1C, CH(Nf)), 130.9 (1C, C(Nf)), 131.2
(1C, C(Nf)), 131.4 (1C, CH(Nf)), 132.1 (2C, C1(Ph)), 135.2 (1C, C(Nf)), 148.7 (2C, C3(Ph)),
152.0 (1C, C(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C_{40}H_{55}N_{6}O_{5}S [M+H]^+ 731.3955; found 731.4005.

5-(10,15-Dioxa-6,19-diaza-3(1,4)-triazacyclononan-1,5(1,4)-dibenzenocyclonadecaphan-
37-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (15c). Obtained from compound 9 (119 mg,
0.17 mmol), dioxadiamine (35 mg, 0.17 mmol), in the presence of Pd(dba)$_2$ (16 mg, 0.0272
mmol), DavePhos (12 mg, 0.0306 mmol), t-BuONa (24 mg, 0.254 mmol), in 10 ml dioxane.
Eluent CH$_2$Cl$_2$ – MeOH 5:1, yield 8 mg (6%), yellow glassy solid. $^1$H NMR (CDCl$_3$) $\delta$
1.17 (br. s, 4H, CCH$_2$CH$_2$C), 1.89 (br. quintet, $^3$J$_{obs}$ = 5.6 Hz, 4H, CCH$_2$C), 2.88 (s, 6H, CH$_3$), 3.10–3.95
(br. m, 16H, CH$_2$N, PhCH$_2$N), 3.24 (br. t, $^3$J$_{obs}$ = 6.2 Hz, 4H, CH$_2$NPh), 3.47 (br. s, 4H, CH$_2$O),
3.57 (br. t, $^3$J$_{obs}$ = 5.4 Hz, 4H, CH$_2$O), 6.57 (d, $^3$J$_{obs}$ = 8.1 Hz, 4H, H$_2$,H$_2$'(Ph)), 7.05 (br. s, 4H,
H3,H3'(Ph)), 7.18 (d, $^3$J$_{obs}$ = 7.5 Hz, 1H, H$_6$(Nf)), 7.51 (t, $^3$J$_{obs}$ = 7.9 Hz, 1H, H3(Nf)), 7.54 (t,
$^3$J$_{obs}$ = 8.3 Hz, 1H, H7(Nf)), 8.04 (br. s, 1H, H2(Nf)), 8.31 (d, $^3$J$_{obs}$ = 9.0 Hz, 1H, H8(Nf)), 8.56 (d,
$^3$J$_{obs}$ = 8.5 Hz, 1H, H4(Nf)), two NH protons were not unambiguously assigned. $^{13}$C NMR
(CDCl$_3$) $\delta$ 27.0 (2C, CCH$_2$CH$_2$C), 29.1 (2C, CCH$_2$C), 42.8 (2C, CH$_2$NPh), 45.4 (2C, CH$_3$), 47.5–
55.0 (br. m, 6C, CH$_2$N), 60.6 (br. s, 2C, $\Delta \nu_{1/2}$ = 140 Hz, PhCH$_2$N), 70.1 (2C, CH$_2$O), 71.0 (2C,
CH$_2$O), 112.8 (4C, C2, C2'(Ph)), 115.5 (1C, CH(Nf)), 118.9 (1C, CH(Nf)), 123.1 (1C, CH(Nf)),
128.6 (1C, CH(Nf)), 130.9 (1C, CH(Nf)), 130.1 (1C, C(Nf)), 130.3 (1C, C(Nf)), 131.0 (1C,
CH(Nf)), 131.7 (4C, C3, C3'(Ph)), 132.2 (2C, C1(Ph)), 135.2 (1C, C(Nf)), 149.1 (2C, C3(Ph)),
152.0 (1C, NC(Nf)). HRMS MALDI-TOF (PEG-600) m/z calcd. for C$_{42}$H$_{59}$N$_{6}$O$_{4}$S [M+H]$^+$
743.4319; found 743.4287.

5-(9,12-Dioxa-6,15-diaza-3(1,4)-triazacyclononan-1,5(1,4)-dibenzenocyclopentadecaphan-
37-ylsulfonyl)-N,N-dimethylnaphthalen-1-amine (15d). Obtained from compound 9 (119 mg,
0.17 mmol), dioxadiamine 13d (25 mg, 0.17 mmol), Pd(dba)$_2$ (16 mg, 0.0272 mmol), DavePhos
(12 mg, 0.0306 mmol), t-BuONa (24 mg, 0.254 mmol), in 10 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH
2:1, yield 6 mg (5%), yellow glassy solid. $^1$H NMR (CDCl$_3$) $\delta$ 2.89 (s, 6H, CH$_3$), 3.10–4.20 (br.
m, 16H, CH$_2$N, PhCH$_2$N), 3.33 (br. s, 4H, CH$_2$NPh), 3.69 (s, 4H, CH$_2$O), 3.76 (t, $^3$J$_{obs}$ = 5.1 Hz,
4H, CH$_2$O), 6.46 (d, $^3$J$_{obs}$ = 8.2 Hz, 4H, H2, H2'(Ph)), 6.98 (br. s, 4H, H3, H3'(Ph)), 7.20 (d,
$^3$J$_{obs}$ = 7.8 Hz, 1H, H6(Nf)), 7.54 (t, $^3$J$_{obs}$ = 7.8 Hz, 1H, H3(Nf)), 7.56 (t, $^3$J$_{obs}$ = 8.3 Hz, 1H,
H7(Nf)), 7.90 (br. s, 1H, H2(Nf)), 8.29 (d, $^3$J$_{obs}$ = 8.5 Hz, 1H, H8(Nf)), 8.58 (d, $^3$J$_{obs}$ = 8.4 Hz, 1H,
H4(Nf)), two NH protons were not unambiguously assigned. HRMS MALDI-TOF (PEG-600)
m/z calcd. for C$_{38}$H$_{59}$N$_{6}$O$_{4}$S [M+H]$^+$ 687.3692; found 687.3725.
5-(10,13,16-Trioxa-3,3,5,5,6,20-pentaaza-3(1,5)-cyclodecana-1,5(1,3)-dibenzenocycloicosaphan-3-ylsulfonfyl)-N,N-dimethylnaphthalen-1-amine (16a). Obtained from compound 10 (113 mg, 0.152 mmol), trioxadiamine 13a (33 mg, 0.152 mmol), in the presence of Pd(dba)2 (14 mg, 0.0243 mmol), DavePhos (11 mg, 0.0274 mmol), tBuONa (58 mg, 0.608 mmol), in 10 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH 10:1, yield 32 mg (26%), yellow glassy solid. UV-vis (CH$_3$CN): $\lambda_{max}$ 305 nm (log$\varepsilon$ 3.59), 340 nm (log$\varepsilon$ 3.43). $^1$H NMR (CDCl$_3$) $\delta$ 1.50–2.70 (br. m, 14H, NCCH$_2$CN, CH$_2$N), 1.87 ( quintet, $^3$J = 6.3 Hz, 4H, NCCH$_2$CO), 2.88 (s, 6H, CH$_3$), 3.10–3.70 (br. m, 20H, CH$_2$O, CH$_2$N, PhCH$_2$N), 3.20 (t, $^3$J = 5.6 Hz, 4H, CH$_2$NPh), 6.44 (d, $^3$J = 7.2 Hz, 2H, H(Ph)), 6.49 (d, $^3$J = 8.2 Hz, 2H, H(Ph)), 6.85 (br. s, 2H, H2(Ph)), 7.05 (t, $^3$J = 7.8 Hz, 2H, H5(Ph)), 7.19 (d, $^3$J = 7.6 Hz, 1H, H6(Ph)), 7.49–7.60 (m, 2H, H3, H7(Ph)), 8.07 (d, $^3$J = 7.3 Hz, 1H, H2(Ph)), 8.41 (br. d, $^3$J = 8.3 Hz, 1H, H8(Ph)), 8.55 (d, $^3$J = 8.2 Hz, 1H, H4(Ph)), two NH protons were not unambiguously assigned. 13C NMR (CDCl$_3$) $\delta$ 25.2 (br. s, 3C, $\Delta$ $\nu_{1/2}$= 30 Hz, NCCH$_2$CN), 29.1 (2C, NCCH$_2$CO), 41.4 (2C, CH$_2$NPh), 45.3 (2C, CH$_3$), 46.9 (br. s, 2C, $\Delta$ $\nu_{1/2}$= 30 Hz, CH$_2$N), 47.7 (br. s, 2C, $\Delta$ $\nu_{1/2}$= 30 Hz, CH$_2$N), 48.5 (br. s, 2C, $\Delta$ $\nu_{1/2}$= 30 Hz, CH$_2$N), 58.7 (2C, PhCH$_2$N), 69.6 (2C, CH$_2$O), 70.2 (2C, CH$_2$O), 70.6 (2C, CH$_2$O), 112.1 (2C, CH(Ph)), 113.6 (2C, CH(Ph)), 115.3 (1C, CH(Ph)), 117.7 (2C, CH(Ph)), 119.3 (1C, CH(Ph)), 123.2 (1C, CH(Ph)), 128.3 (1C, CH(Ph)), 129.4 (2C, CH(Ph)), 129.6 (1C, CH(Ph)), 130.1 (1C, C(Ph)), 130.3 (1C, C(Ph)), 130.7 (1C, CH(Ph)), 133.6 (br. s, 1C, C(Ph)), 149.3 (2C, C3(Ph)), 151.9 (1C, NC(Ph)), quaternary carbon atom C1(Ph) was not unambiguously assigned. HRMS MALDI-TOF (PEG-600 + PEG-1000) m/z calcd. for C$_{45}$H$_{65}$N$_6$O$_5$S [M+H]$^+$ 801.4737; found 801.4761.

(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}propyl){3-[(5,9-bis{[5-(dimethylamino)-1-naphthyl]sulfonyl}-1,5,9-triazacyclododecan-1-yl)methyl]phenyl}amine (17). Obtained from compound 9 (161 mg, 0.2 mmol), trioxadiamine 13a (22 mg, 0.1 mmol), in the presence of Pd(dba)$_2$ (18 mg, 0.032 mmol), BINAP (22 mg, 0.036 mmol), tBuONa (58 mg, 0.6 mmol), in 1.5 ml dioxane. Eluent CH$_2$Cl$_2$ – MeOH 2:1, yield 21 mg (22%), yellow viscous oil. UV-vis (CH$_3$CN): $\lambda_{max}$ 305 nm (log$\varepsilon$ 3.62), 340 nm (log$\varepsilon$ 3.48). $^1$H NMR (CDCl$_3$) $\delta$ 1.85 (br. s, 4H, CCH$_2$C), 1.93 (quintet, $^3$J = 6.4 Hz, 4H, CCH$_2$C), 2.09 (br. s, 2H, CCH$_2$C), 2.71 (br. s, 4H, CH$_2$N), 2.86 (s, 12H, CH$_3$), 3.12 (t, $^3$J = 5.4 Hz, 2H, CH$_2$NH$_2$), 3.22 (t, $^3$J = 6.3 Hz, 2H, CH$_2$NPh), 3.25 (t, $^3$J = 5.6 Hz, 4H, CH$_2$N), 3.31 (t, $^3$J = 6.6 Hz, 4H, CH$_2$N), 3.50–3.66 (m, 12H, CH$_2$O, PhCH$_2$N), 3.67 (t, $^3$J = 6.1 Hz, 2H, CH$_2$O), 6.50 (d, $^3$J = 7.2 Hz, 1H, H(Ph)), 6.60 (dd, $^3$J = 8.0 Hz, $^4$J = 1.8 Hz, 1H, H(Ph)), 6.83 (br. s, 1H, H2(Ph)), 7.06 (t, $^3$J = 7.6 Hz, 1H, H5(Ph)), 7.16 (d, $^3$J = 7.7 Hz, 2H, H6(Ph)), 7.49 (dd, $^3$J = 8.5 Hz, $^3$J = 7.5 Hz, 2H, H3(Ph)), 7.52 (dd, $^3$J = 8.7 Hz, $^3$J = 7.7 Hz, 2H, H7(Ph)), 8.06 (dd, $^3$J = 7.5 Hz, $^4$J = 1.0 Hz, 2H, H2(Ph)), 8.32 (d, $^3$J = 8.7 Hz, 2H,
H8(Nf)), 8.52 (d, $J = 8.5$ Hz, 2H, H4(Nf)), NH and NH$_2$ protons were not unambiguously assigned. $^{13}$C NMR (CDCl$_3$) $\delta$ 25.9 (2C, CCH$_2$C), 28.9 (2C, CCH$_2$C), 29.7 (1C, CCH$_2$C), 40.3 (1C, CH$_2$NH$_2$), 41.7 (1C, CH$_2$NPh), 45.4 (4C, CH$_3$), 46.1 (2C, CH$_2$N), 46.6 (br. s, 4C, $\Delta\nu_{1/2}>100$ Hz, CH$_2$N), 59.1 (1C, PhCH$_2$N), 69.5 (1C, CH$_2$O), 69.6 (2C, CH$_2$O), 69.9 (1C, CH$_2$O), 70.4 (1C, CH$_2$O), 70.5 (1C, CH$_2$O), 114.4 (1C, CH(Ph)), 115.3 (1C, CH(Ph)), 115.4 (2C, CH(Nf)), 118.6 (1C, CH(Ph)), 119.2 (2C, CH(Nf)), 123.2 (2C, CH(Nf)), 128.4 (2C, CH(Nf)), 129.4 (1C, C5(Ph)), 129.7 (2C, CH(Nf)), 130.1 (2C, C(Nf)), 130.3 (2C, C(Nf)), 130.7 (2C, CH(Nf)), 133.4 (2C, C(Nf)), 149.2 (1C, C3(Ph)), 151.8 (2C, NC(Nf)), quaternary carbon atom C1(Ph) was not unambiguously assigned. HRMS MALDI-TOF (PEG-1000) m/z calcd. for C$_{50}$H$_{72}$N$_{7}$O$_{7}$S$_{2}$ [M+H]$^+$ 946.4935; found 946.4872.
$^1$H NMR spectrum of compound 14a in CDCl$_3$ at 298 K.

$^1$H NMR spectrum of compound 14a in DMSO-$d_6$ at 298 K.

$^1$H NMR spectrum of compound 14a in DMSO-$d_6$ at 363 K.

Figure S1. $^1$H NMR spectra of compound 14a in different solvents at different temperatures.
Figure S2. UV-vis spectra of the ligand 14a in the presence of different metals (5 equiv.).

Figure S3. UV-vis spectra of the ligand 14b in the presence of different metals (5 equiv.).
Figure S4. Fluorescence spectra of the ligand 14b in the presence of different metals (5 equiv.).

Figure S5. Fluorescence spectra of compound 14c in the presence of different metals (5 equiv.).
Figure S6. Fluorescence spectra of the ligand 14d in the presence of different metals (5 equiv.).

Figure S7. Fluorescence spectra of the ligand 15a in the presence of different metals (5 equiv.).
Figure S8. Fluorescence spectra of the ligand 16a in the presence of different metals (5 equiv.).

Figure S9. Fluorescence spectra of the ligand 17 in the presence of different metals (5 equiv.).
References.