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Amidetriazole: A Versatile Building Block for Construction of Oxyanion Anion Receptors

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Abstract: The design and synthesis of efficient receptors for tetrahedral oxyanions is an emerging field in supramolecular chemistry. Herein, we have developed a urea-like anion-recognizing motif, amidetriazole, which can be easily synthesized and derived and shows good solubility. A series of simple acyclic receptors were designed and synthesized to confirm the potential of amidetriazole for the construction of tetrahedral oxyanion receptors. This molecular platform can be used extensively for the construction of numerous receptor systems appended with functional groups, which opens the way to many applications in the field of supramolecular chemistry.

Keywords: amidetriazoles · anions · click chemistry · host–guest systems · receptors

Introduction

Tetrahedral oxyanions are prominent radioactive contaminants (e.g., pertechnetate), toxic or otherwise troublesome species (e.g., sulfate, chromate, arsenate, and phosphate, to name a few), or matrix elements that can interfere with proposed waste-treatment processes.[1] The design and synthesis of efficient receptors for tetrahedral oxyanions is an important field in supramolecular chemistry.[2] Anion receptors with amide, pyrrole, urea, ammonium, imidazolium, and guanidinium groups as binding sites for tetrahedral oxyanions have been widely studied.[3] The urea moiety has been utilized effectively in a number of tetrahedral oxyanion binding systems.[2a] The synthesis of urea derivatives involves the toxic reagents isocyanate or phosgene. Unsymmetrical urea derivatives are relatively difficult to obtain.[4] As a result, a building block with slight structural variation but similar functionality to the urea moiety is desirable for construction of artificial receptors for tetrahedral anions. 1,2,3-Triazoles with 5 Debye (D) dipole character are new motifs that can participate in multiple noncovalent interactions (for example, anion recognition[5] within flexible[6] and shape-persistent triazolophanes[7] and in foldamers)[8] and they can help facilitate self-assembly.[9] 1,2,3-Triazoles can serve as a surrogate for amide bonds,[10] which motivated us to replace one of the amide NH groups in the urea moiety with 1,2,3-triazole to generate a versatile anion-receptor building block that combines the characteristics of urea and triazole; that is, amidetriazole (Figure 1b). This building block has enormous advantages, such as ease of preparation, especially for the construction of asymmetric molecules for functional purposes.

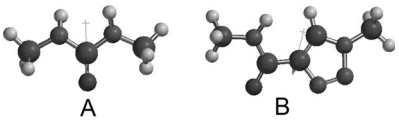

Figure 1. Molecular modeling of a) tetramethylurea and b) amidetriazole (HF 6-31G**).

Results and Discussion

The synthesis of amidetriazole can be achieved through two strategies: 1) Huisgen 1,3-dipolar cycloaddition between methyl propiolate and a substituted azide followed by aminolysis with amines (Scheme 1a) or 2) formation of N-substituted propiolamide through condensation of propiolic acid and amines followed by Cu^{I}-catalyzed cycloaddition (Scheme 1b). Molecular modeling (HF 6-31 G**) indicated that amidetriazole exhibits a distance of 2.27 Å between the amide NH and triazole CH groups when it adopts an anion-binding conformation. Amidetriazole is structurally similar

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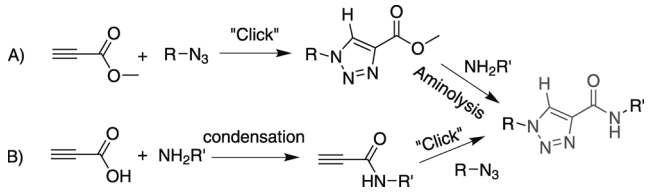


Scheme 1. Strategies for the synthesis of amidetriazole.

to tetramethylurea and has a larger dipole (7.89 versus 4.71 D). The structure of the amidetriazole unit is further illustrated by the X-ray structure of model compound **1** (Figure 2). For the free amidetriazole motif, the amide NH

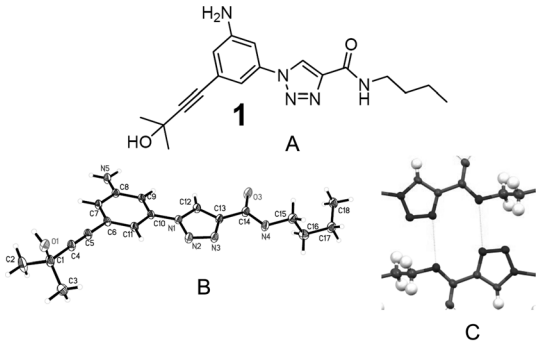


Figure 2. a) Molecular structure of amidetriazole-containing model compound **1**; b) Crystal structure of model compound **1**; c) Two-point hydrogen bonds formed by the amide NH group and the triazole nitrogen atoms in a dimer of **1** in the crystal structure.

and triazole CH units occupy opposite positions relative to one another (Figure 2b), the N–N=N triazole unit preferentially forms an intermolecular hydrogen bond with the amide NH group (N···N distance = 3.035 Å; Figure 2c). The amidetriazole unit can resolve the poor solubility of the urea moiety through the formation of a dimer rather than the polymer-like assembly of ureas.

Furthermore, we designed and synthesized a series of simple, acyclic receptors to confirm the potential of amidetriazole for the construction of tetrahedral oxyanion receptors (Figure 3). The conformations of these receptors are controlled by either a V-shaped carbazole or tripodal 2,4,6-triethylbenzene, and the terminal hydroxyl group on the chain will provide additional anion-binding affinity. A more elaborate example is the incorporation of hydrogen bonding, π–π stacking, and dipole–dipole interactions for the realization of anion binding. These receptors are synthesized as illustrated in Schemes 2–4.

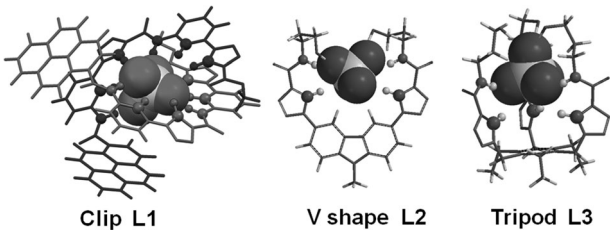
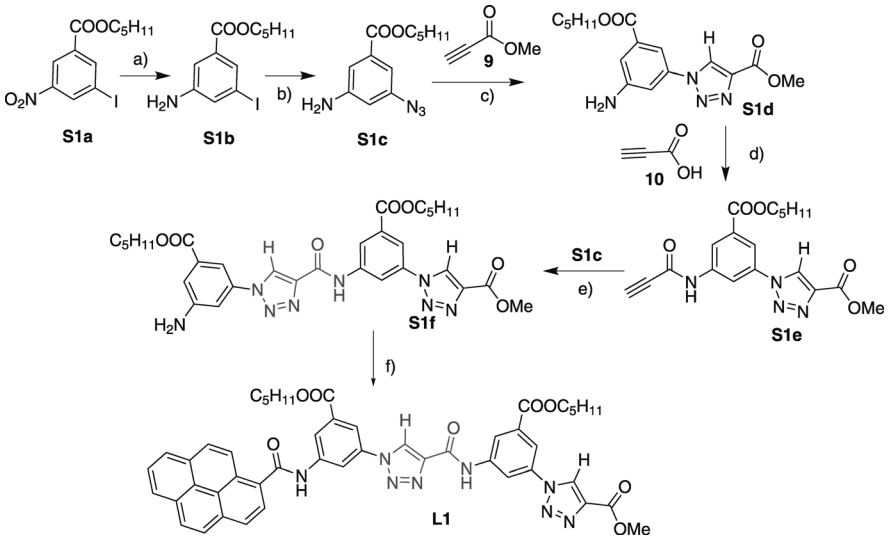


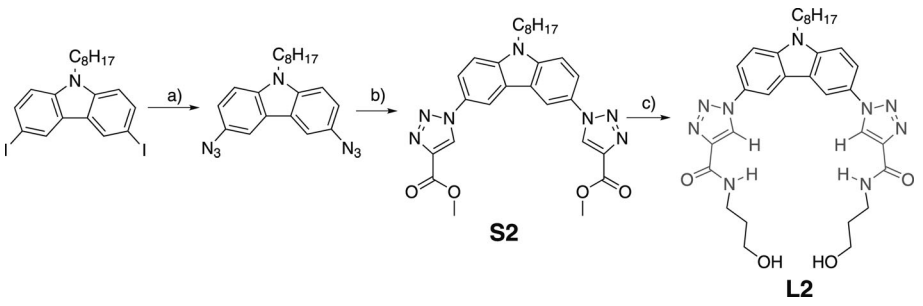
Figure 3. Tetrahedral oxyanionic receptors designed based on different preorganization strategies.

Sulfate is the smallest common tetrahedral anion and plays important roles in biological systems and disease,[11] in hydrometallurgy,[12] and as a pollutant.[13] Custelcean and co-workers developed selective receptors for sulfate-based tripodal tris-urea systems for precipitation of anions from solution.[14] Custelcean, Hay, and co-workers have used self-assembly strategies to construct urea-containing cage systems with six urea groups arranged around sulfate.[15] Gale obtained some sulfate-selective acyclic receptors based on indole and carbazole.[16] Beer and Mullen utilized sulfate as a template to prepare interlocked structures.[17] Macrocyclic sulfate receptors such as cyclo[8]pyrrole,[18] cyclic tetraamide/amine-based receptors,[19] and cyclic peptide-based molecular oysters[20] were also reported. The binding behavior of our sulfate receptors will be studied.

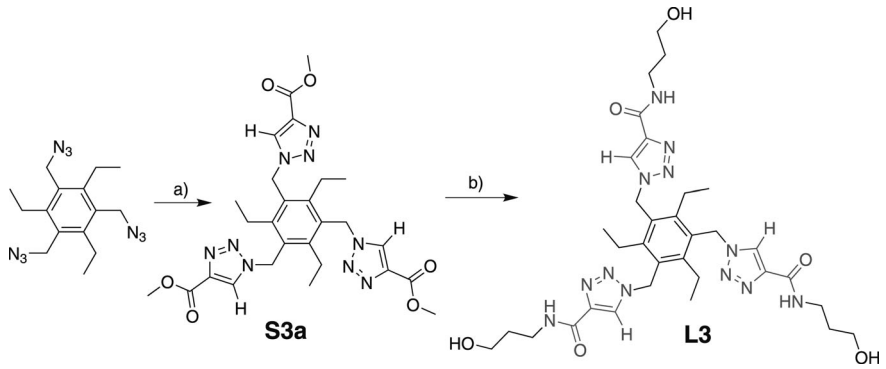
In our preliminary endeavor to build foldamers by using the amidetriazole motif, we designed a new sulfate receptor, **L1**, with an amidetriazole unit in the middle, another amide



Scheme 2. Preparation of **L1**. Reaction conditions: a) $SnCl_2$, ethanol, 81%; b) NaN_3, sodium ascorbate, CuI, *N,N'*-dimethylethane-1,2-diamine, DMSO/H_2O (5:1), RT, 1 h, 81%; c) $CuSO_4$, sodium ascorbate, ethanol/H_2O (2:1), RT, 8 h, 88%; d) *N,N*-dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine (DMAP), CH_2Cl_2, 76%; e) $CuSO_4$, sodium ascorbate, ethanol/H_2O (2:1), RT, 8 h, 67%; f) Pyrene-1-carboxylic acid chloride, NEt_3, 63%.



Scheme 3. Preparation of **L2**. Reaction conditions: a) NaN_3, sodium ascorbate, CuI, *N*,*N*'-dimethylethane-1,2-diamine, DMSO/H_2O (5:1); b) Methyl propiolate, $CuSO_4$, sodium ascorbate, ethanol/H_2O (2:1), RT, 8 h, 85% over two steps; c) 3-Aminopropan-1-ol, toluene, 80°C, 10 h, 81%.



Scheme 4. Reaction conditions: a) Methyl propiolate, $CuSO_4$, sodium ascorbate, ethanol/H_2O (2:1), RT, 8 h, 95%; b) 3-Aminopropan-1-ol, toluene, 80°C, 10 h, 90%.

group, and a triazole unit connected with benzene rings, in which the binding affinity of the amidetriazole and its individual components can be compared. The photoactive pyrene ring is attached to the amide terminal as a fluorescent handle and provides π–π stacking; the triazole terminal is equipped with a carboxylate group to increase the acidity of the triazole CH proton relative to the amidetriazole CH proton. Molecular modeling indicated that the two amide NH and two triazole CH groups combined with the CH of the connecting benzene group can interact with a sulfate anion in a 1:1 or 2:1 ratio, to form six or twelve hydrogen bonds, respectively.

Upon the addition of 0.5 equivalents of bis(tetrabutylammonium) sulfate (TBA_2SO_4), the triazole proton of the middle amidetriazole unit ($\Delta\delta H_g = 1.61$ ppm) and the amide proton ($\Delta\delta H_f = 1.01$ ppm) showed downfield shifts. The upfield shifts of protons H_r and H_s on the pyrene ring and alkyl chain, respectively, and H_h on the benzene ring close to the pyrene ring is evidence for the 2:1 binding mode, which can provide strong shielding effects to these protons. Small upfield shifts of protons H_k, H_j, and H_e are also observed. With the addition of another 0.5 equivalents of sulfate (1.0 equiv total), the signals of the central amide NH (H_f) and triazole CH (H_g) protons migrated further downfield and the upfield-shifted signals H_r, H_s, and H_h moved back to their original position (Figure 4, middle). With the addition of more sulfate (5 equiv), the signals of protons H_g and H_b were sharpened, whereas H_f and H_k disappeared. These results clearly indicate that the addition of sulfate to a solution of host **L1** leads to the predominant formation of a 2:1 host–guest complex at the initial stages of the titration up to the sulfate/**L1** ratio of 0.5. This complex is gradually replaced by a 1:1 complex as the sulfate/**L1** ratio increases from 0.5 to 1 and, ultimately, the 1:1 complex prevails thereafter.[21] Large binding constants (K_1 and K_2) are anticipated from the appearance of sharp changes in curvature at sulfate/**L1** ratios of 1:2 and approximately 1:1, even though the binding constants cannot be obtained through ^{1}H NMR titration data due to line broadening. The binding affinity of amidetriazole is definitely higher than that of its individual component, which is supported by the small downfield shift of the terminal triazole proton. To obtain deeper insight for the sulfate-induced 2:1 folding, NOESY NMR spectroscopy and molecular modeling were carried out for the structural assignment of the sulfate complex in solution (Figure 4, bottom). Strong NOE connections were exhibited between H_s and H_k, H_t, and H_k, H_k and H_j, H_k and H_g, H_j and H_f, H_g and H_e, and H_f and H_b, which supported the formation of the folded half-circle conformation. NOE connections were clearly observed between the signals of the middle (H_g) and terminal triazole protons (H_b), and also with the terminal pyrene unit (H_s, H_t; see the circled cross peaks in Figure 4, bottom). Because distances between H_g and H_b, H_s, and H_t of the same chain are much too long for any cross peak to be observed these signals must correspond to intermolecular contacts between different chains.[22] This is precisely the situation when the two chains wrap around each other (Figure 4, top,c). This complex is stabilized by π–π stacking between the pyrene unit and the close phenyl-triazole plane in the second molecule and by dipole–dipole interactions between the terminal phenyl (−2 D) and triazole groups (+5 D) (Figure 4, top,c).[23] This can explain the small downfield shift of triazole proton H_b and even the upfield shift of the terminal amide proton H_k, which is the sum of π–π stacking (upfield shift) and hydrogen-bonding interactions (downfield shift). Dihydrogen phosphate can form a similar 1:2 complex with **L1**, supported by the upfield shift of the related aromatic protons, although detailed analysis

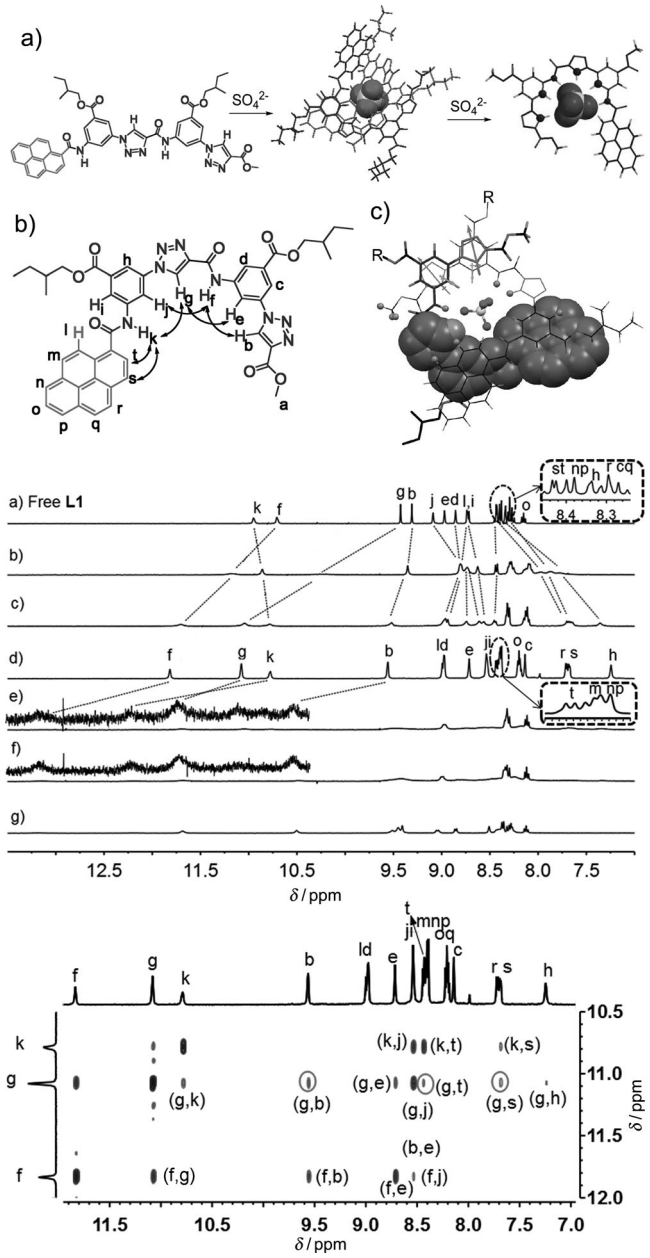


Figure 4. Top: a) Illustration of the sulfate-binding process of receptor **L1**; b) Intramolecular NOE contact in the $\mathbf{L1}_2$·SO_4 complex; c) Molecular modeling of the $\mathbf{L1}_2$·SO_4 complex and the intermolecular NOE contacts. Middle: ^{1}H NMR ([D$_6$]acetone/0.5% [D$_6$]DMSO, 400 MHz) spectra of **L1** (5 mM) in the presence of SO_4^{2-} ions (0.25, 0.5, 0.5 at 243 K, 0.75, 1.0, and 5.0 equiv for b) to g), respectively). Bottom: Partial NOESY spectrum (600 MHz) of **L1**+SO_4^{2-} in [D$_6$]acetone/0.5% [D$_6$]DMSO at 243 K (mixing time = 1 s).

was prevented by line broadening (Figure S2 in the Supporting Information).

UV/Vis experiments were carried out in acetone to evaluate the binding properties of **L1** towards sulfate (Figure S11 in the Supporting Information). Upon addition of sulfate, the absorption at $\lambda = 274$ nm first decreases to a minimum in the presence of 0.5 equivalents of sulfate as a consequence of the π-stacked structure in the 2:1 host–guest complex.[23] The absorbance then increases with the addition of more sulfate until the 1:1 complex is dominant. The absorption at $\lambda = 365$ nm behaves reversely, increasing then dropping, which corresponds to the formation and destruction of π–π stacking between the pyrene ring and phenyl-triazole planes. These changes of **L1** reflect structural reorganization due to the binding of sulfate, consistent with the above ^{1}H NMR results. **L1** exhibits an emission band at $\lambda = 400$ nm, which is quenched by the addition of SO_4^{2-} (Figure S11 in the Supporting Information).

Encouraged by the fact that two amidetriazole molecules can form a 2:1 complex with sulfate, we coupled our amidetriazoles on the 3,6-positions of a carbazole moiety to build receptor **L2** with two amide NH, two triazole CH, and two OH groups present for hydrogen-bond formation. Carbazole and its derivatives have been widely used as functional building blocks in the fabrication of organic photoconductors, nonlinear optical materials, and photorefractive materials due to their specific optical and electrochemical properties.[24] At the same time, the 6 Å distance between the C3 and C6 carbon atoms and the V-shape generated upon 3,6-modification rendered carbazole with the potential to control the geometry of the receptors.

The complexation behavior of host **L2** with the sulfate anion was studied by ^{1}H NMR titration in [D$_6$]acetone/5% [D$_6$]DMSO at 25 °C. Upon addition of 1 equivalent of sulfate, large downfield shifts of the amide NH ($\Delta\delta H_e = 1.24$ ppm), triazole ($\Delta\delta H_d = 1.71$ ppm), and hydroxyl group resonances ($\Delta\delta H_i = 2.49$ ppm) were observed (Figure 5). The stable 1:1 complex allowed for a structural investigation in solution by using NOESY NMR spectroscopy. Strong NOE connections were exhibited between H_d and H_a and H_d and H_e (Figure S17 in the Supporting Information), which supported the conformation of the amidetriazole moieties within a carbazole unit, shown in Figure 5. Interestingly, the carbazole proton H_a first shifted downfield ($\Delta\delta = 1.09$ ppm) almost proportionally to the amount of added sulfate until the sulfate/**L2** ratio reached 1:1, shifted back upfield until the ratio reached 6.3:1, and finally leveled off (Figure 5, bottom). The signal of proton H_c started to move downfield after the addition of 1 equivalent of sulfate. These results clearly indicate that the two amidetriazole arms can cooperatively capture one sulfate anion at first, then with the addition of more sulfate (6.3 equiv) the C–N bond connecting one of the triazole and carbazole rings rotates so that each arm can bind one sulfate anion (Figure 5). The hydrogen-bonding interactions between proton H_a and sulfate were decreased, whereas hydrogen-bonding interactions between proton H_c and sulfate were increased; a weak complex with 1:2 host–guest stoichiometry was formed. The binding constant (K_1) of the first sulfate can be fitted from proton H_d ($K_1 = 3895\ M^{-1}$). Dihydrogen phosphate binds with **L2** in a similar way but with lower stability (Figure S4 in the Supporting Information).

The binding affinity will increase with the addition of binding moieties and strength of the preorganization. Tripo-

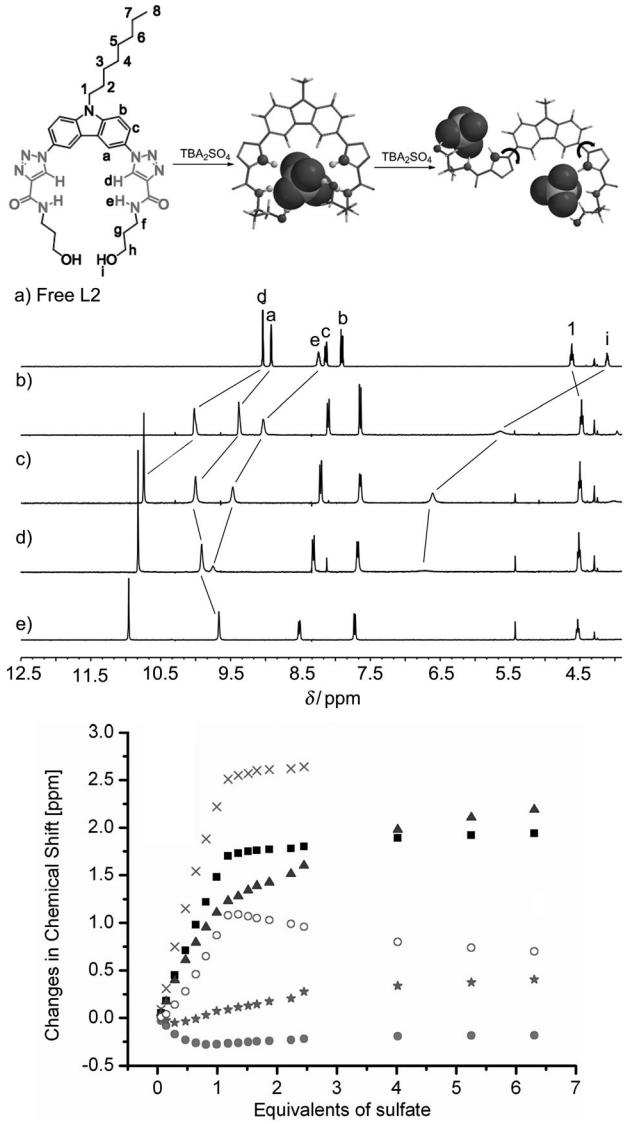


Figure 5. ^{1}H NMR ([D$_6$]acetone/0.5% [D$_6$]DMSO, 400 MHz) spectra of **L2** (5 mM) in the presence of SO_4^{2-} ions (0.5, 1.0, 2.0, and 5.0 equiv for b) to e), respectively) and the titration curves (H_a ○, H_b ●, H_c ★, H_d ■, H_e ▲, H_i ×).

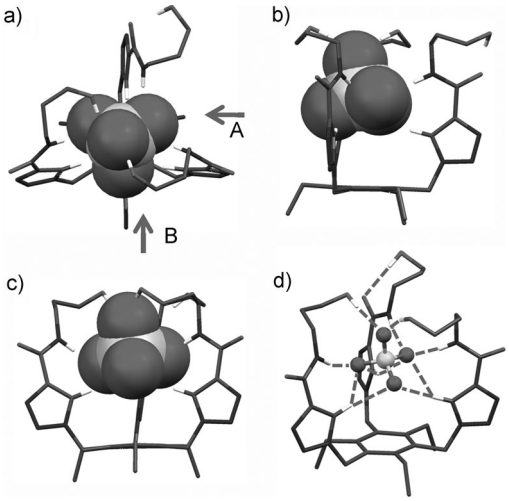


Figure 6. Crystal structure of the sulfate complex **L3**·SO_4 (non-acidic hydrogen atoms and countercations omitted for clarity). a) Top view; b),c) Side view from directions A and B shown in a); d) Hydrogen bonds around SO_4^{2-}.

dal receptor **L3** was designed based on the "pinwheel" scaffold 1,3,5-trisubstituted-2,4,6-triethylbenzene.[25] Preorganization is achieved by incorporation of three amidetriazole groups into a 1,3,5-triethylbenzene core, to generate a cone-shape cavity. The introduction of steric bulk around the benzene-derived core predisposes the compound to adopt the preferred conformation.[25] We obtained single crystals of a sulfate complex of **L3** for X-ray analysis by diffusing ether into a solution of **L3** and TBA_2·SO_4 in acetone/5% DMSO (Figure 6). **L3** shows high conformational complementarity with the sulfate anion in the 1:1 host–guest complex; three amide NH, three triazole CH, and two terminal OH groups can be involved in hydrogen bonding with the sulfate to form 11 hydrogen bonds. The N···O distances ranged from 2.831–2.906 Å (2.869 Å on average) and N–H···O angles from 163.2–172.1° (164.11° on average); the C···O distances ranged from 3.095–3.292 Å (3.129 Å on average) and C–H···O angles from 123.53–168.67° (154.11° on average); the O···O distances ranged from 2.731–2.749 Å (2.734 Å on average) and O–H···O angles from 160.3–161.2° (160.51° on average).[26]

The interaction of receptor **L3** with sulfate anions was further investigated in [D$_6$]acetone/5% [D$_6$]DMSO by using a ^{1}H NMR titration technique. The receptor–anion stoichiometries were determined by a continuous variation method (Job plots) and proved to be 1:1 for sulfate anions. The addition of sulfate anions to 2.5 mM solutions of receptor **1** in [D$_6$]acetone/5% [D$_6$]DMSO led to large downfield shifts of the amide NH ($\Delta\delta H_e = 1.94$ ppm), triazole proton ($\Delta\delta H_d = 1.25$ ppm), and terminal hydroxyl group resonances ($\Delta\delta H_i = 1.72$ ppm) (Figure 7). These large downfield shifts indicate that the sulfate anion forms strong hydrogen bonds with all binding sites of the tripodal receptor. The stability constant of the sulfate complex of **L3** could only be determined by analysis of the signal shifts of benzylic proton H_c because of line broadening of the binding-site proton signals in the ^{1}H NMR spectrum. The data was fitted with the WinEQNMR2 software[27] to give $K_1 > 100\,000$.

Of these representative foldamer-type, cleft-type, and tripodal receptors that contained amidetriazole groups, the third receptor **L3** forms 1:1 complexes with sulfate anions that have remarkably high stability, the other two receptors additionally form complexes of higher stoichiometry. We expanded the anion-binding studies of receptor **L3** to investigate oxyanion selectivity. Addition of tetrabutylammonium iodide to **L3** in [D$_6$]acetone/0.5% [D$_6$]DMSO resulted in only very small perturbations in the ^{1}H NMR spectra. For chloride and bromide ions the triazole motifs supply stronger C–H···halide bonds than the amide N–H···halide bonds, evidenced from the larger chemical shifts of the resonance

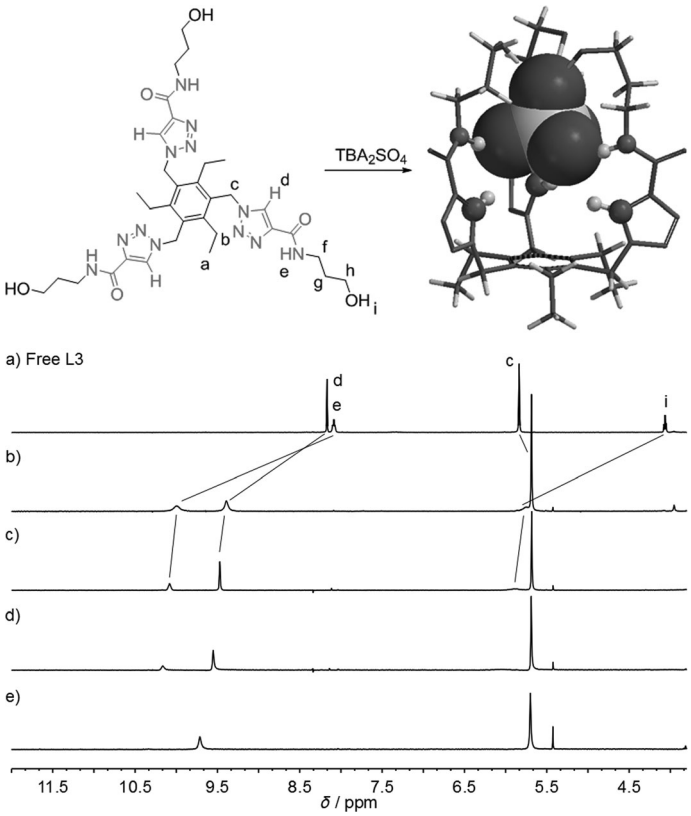


Figure 7. ^{1}H NMR ([D$_6$]Acetone/0.5 % [D$_6$]DMSO, 400 MHz) spectra of **L3** (2.5 mM) in the presence of SO_4^{2-} ions (1.0, 2.0, 3.0, and 7.0 equiv for b) to e), respectively).

of proton H$_d$ relative to H$_e$ (Figures S8 and S9 in the Supporting Information). The opposite trends were observed for oxyanionic anions, that is, the amides formed stronger N−H···O bonds than the C−H···O bonds to the triazole units (Figures S6 and S10 in the Supporting Information). The resonance of the terminal OH group shifted downfield with the addition of halide, whereas it disappeared in the presence of oxyanions. The titration results indicated that halides (Cl^-, Br^-) mainly interacted with the triazole CH unit, whereas oxyanions interacted with the NH, CH, and OH groups cooperatively. The binding constants (K_1 only) for the first anion derived from a model incorporating a final host–guest stoichiometry of 1:3 are summarized in Table 1. The analysis was carried out with the aid of WinEQNMR2 software.[27] With increasing halide size, the binding stability decreased. In the oxyanions studied, **L3** showed the greatest selectivity towards sulfate, with an affinity too high to measure in the chosen medium ($K_1 > 100000\,M^{-1}$).

Table 1. Binding constants (K_1) determined by ^{1}H NMR titration for the interaction of **L3** with various anions.[a]

Anion	$F^-\cdot 3H_2O$	Cl^-	Br^-	I^-	CH_3COO^-	$H_2PO_4^-$	SO_4^{2-}
K_1	581	186	16	–[b]	106	292	>100000[c]

[a] Anions as nBu_4N^+ salts in [D$_6$]acetone/0.5 % [D$_6$]DMSO, triazole protons H$_d$ fit with WinEQNMR2.[27] Errors in K_1 are <10 %. Equilibria were modeled according to the binding of up to three anions by each host. [b] Only small perturbations were observed in the ^{1}H NMR spectrum upon addition of iodide anions. [c] Fitting followed with benzyl proton H$_e$ because of the line broadening of the binding-site proton signals in the NMR spectra.

An interesting phenomenon was observed for fluoride binding. With the addition of tetrabutylammonium fluoride (TBA-F) trihydrate to a solution of **L3** in [D$_6$]acetone/0.5 % [D$_6$]DMSO, larger chemical shifts were observed for the resonance of amide proton H$_e$ relative to that of triazole proton H$_d$. The 1:1 binding stoichiometry was obtained from proton H$_d$, whereas a final host–guest stoichiometry of 1:3 was achieved from proton H$_e$. Uncommonly, a new ^{1}H NMR resonance at $\delta = 8.11$ ppm appeared, which reached the highest level at 1.57 equivalents of hydrated fluoride and decreased with the addition of more hydrated fluoride (Figure 8a and b). This new peak was assigned as H_2O bound to fluoride and the integration of this peak relative to proton H$_d$ showed a 4:1 ratio to **L3**. The results indicated that tripodal **L3** first formed a 1:1 complex with hydrated fluoride, followed by a 1:3 complex with fluoride. ^{19}F NMR was used to investigate fluoride anion binding by the receptor **L3**. The addition of **L3** to a solution of TBA-F trihydrate in [D$_6$]acetone/0.5 % [D$_6$]DMSO resulted in a downfield shift of $\delta = 4.46$ ppm relative to the free fluoride resonance (Figure 8c), which results from the weakened hydrogen bonding between fluoride and water, indicative that the fluoride anion does not directly participate in hydrogen bonding with the −CH and −NH groups of the receptor **L3**.[28] These results led to the binding model presented in Figure 8d. The water molecules formed a hydrogen-bond network with the middle fluoride ion and outer C=O groups, and the triazole CH and terminal OH groups provided further stabilization to the top water molecule through O−H···O interactions. The hydrated fluoride functioned as a pseudo-oxyanion and showed relatively strong binding with **L3**.

Conclusion

We have developed a urea-like anion-recognizing motif, amidetriazole, which can be easily synthesized and derivatized and shows good solubility. This molecular platform can be used extensively for the construction of numerous receptor systems appended with functional groups. These systems can open the way to many applications, for example, in the field of addressable sensors or display. The studies demonstrated that rational design with the cooperation and preorganization of the amidetriazole units can lead to quite strong oxyanion receptors. We are currently developing more preorganized receptors that contain amidetriazole units, such as macrocycles, as more practical and selective chemosensors for oxyanions.

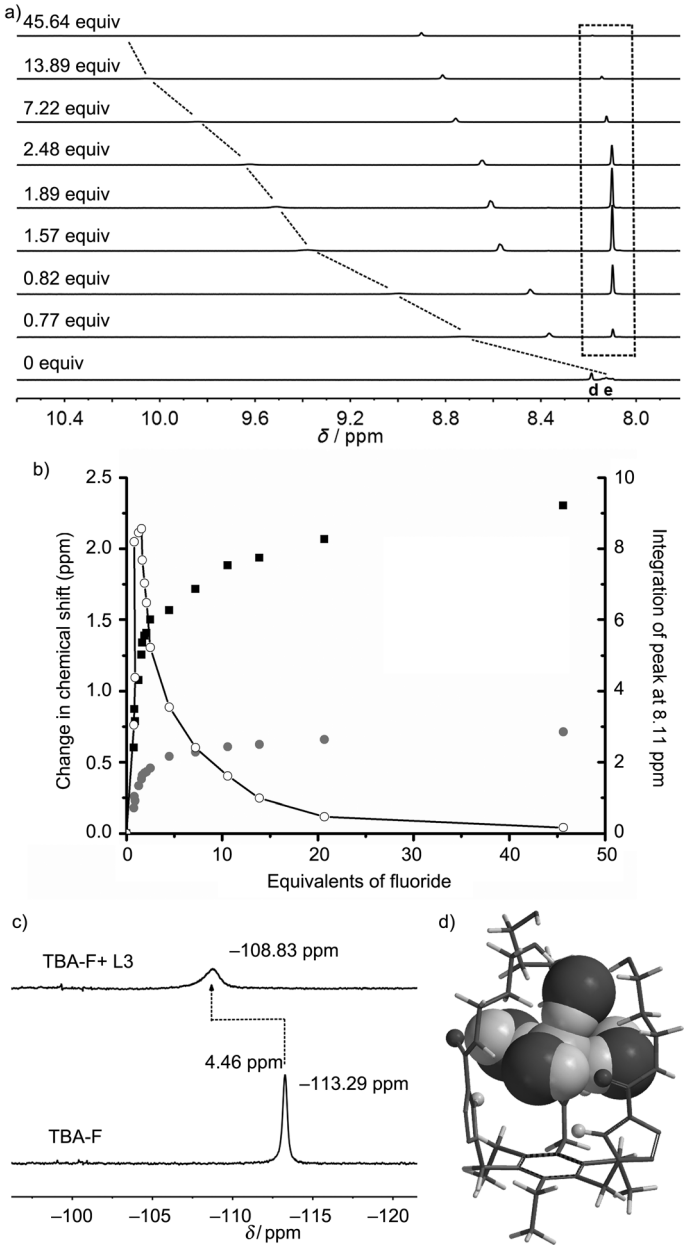


Figure 8. a) ^{1}H NMR ([D$_6$]/acetone/0.5% [D$_6$]DMSO, 400 MHz) spectra of **L3** (2.5 mM) in the presence of TBA-F·3H$_2$O; b) Titration curves; CH ●, NH ■, (the integration of the peak at $\delta = 8.11$ ppm (○) is calibrated with proton H$_d$); c) Partial ^{19}F NMR spectra (400 MHz) of TBA-F and a 1:1 mixture of **L3** and TBA-F in [D$_6$]acetone/0.5% [D$_6$]DMSO at 298 K; d) Binding model of **L3** with hydrated fluoride.

Experimental Section

General methods: All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160–200 mesh) and TLC was performed on precoated silica gel plates and observed under UV light. NMR spectra were recorded on Bruker Avance DPS-400 and Bruker Avance DPS-600 spectrometers at room temperature (298 K). Chemical shifts were referenced to the residual-solvent peaks. MALDI-TOF mass spectrometry was performed on a Bruker Biflex III mass spectrometer. Electronic absorption spectra were measured on a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500. All single crystal X-ray diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 173 K. Intensities were corrected for absorption effects using the multi-scan technique SADABS (Siemens area detector absorption corrections). The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F2 by using the SHELXL 97 program (Sheldrick, 1997). The extended packing plots and data from crystal packing were obtained with Mercury 1.4.1 software.

Compound S1a: DMF (1 drop) was added to a solution of 3-iodo-5-nitrobenzoic acid (2.93 g, 10 mmol) in $SOCl_2$ (5 mL) and the mixture was stirred at 50 °C for 2 h. The solvent was removed under vacuum. The residue was dissolved in dry CH_2Cl_2 (5 mL) and added dropwise to a solution of 2-methylbutan-1-ol (1 g, 12 mmol) and triethylamine (TEA) (3 mL) in dry CH_2Cl_2 (20 mL). The mixture was stirred at RT for 4 h. The solvents were removed under vacuum and the residue was dissolved in CH_2Cl_2 then washed with brine. The organic phase was dried (Na_2SO_4) and the solvent was removed under vacuum. The product was purified by chromatography (SiO_2, hexane) to give **S1a** (3 g, 82.6%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.79$ (s, 1H), 8.73 (s, 1H), 8.66 (s, 1H), 4.28 (m, 1H), 4.18 (m, 1H), 1.90 (m, 1H), 1.54 (m, 1H), 1.29 (m, 1H), 1.03 (d, $J =$ 8 Hz, 3H), 0.97 ppm (t, $J = 8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 163.2, 148.6, 144.0, 136.0, 133.6, 123.8, 93.4, 70.9, 34.3, 26.1, 16.5, 11.3 ppm; MS (EI): m/z: 363; elemental analysis calcd (%) for ($C_{12}H_{14}INO_4$): C 39.69, H 3.89, N 3.86; found: C 39.38, H 3.92; N 3.89.

Compound S1b: $SnCl_2$·2H$_2$O (9.06 g, 40.0 mmol) was added to a solution of **S1a** (2.9 g, 8 mmol) in ethanol (5 mL). The reaction mixture was heated at reflux until the reaction was complete (indicated by TLC analysis). The solvent was removed under reduced pressure and the crude residue was partitioned between ethyl acetate and 2 M KOH. The aqueous layer was extracted with ethyl acetate (3×25 mL) and the combined organic extracts were washed with brine (2×25 mL) and water (3×50 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude residue was subjected to flash silica gel column chromatography (20% ethyl acetate in hexanes) to yield **S1b** (81%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.74 (s, 1H), 7.31 (s, 1H), 7.23 (s, 1H), 4.17 (dd, $J = 10.7$, 6.0 Hz, 1H), 4.09 (dd, $J = 10.7$, 6.7 Hz, 1H), 1.84 (dq, $J = 13.2$, 6.7 Hz, 1H), 1.58–1.44 (m, 1H), 1.34–1.19 (m, 1H), 1.00 (d, $J = 6.7$ Hz, 2H), 0.95 ppm (t, $J =$ 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.5$, 147.7, 133.1, 128.3, 127.6, 115.4, 94.5, 70.0, 34.4, 26.2, 16.6, 11.4 ppm; MS (EI): m/z: 333; elemental analysis calcd (%) for ($C_{12}H_{16}INO_2$): C 43.26, H 4.84, N 4.20; found: C 43.14, H 4.72, N 4.31.

Compound S1c: Compound **S1b** (1.33 g, 4 mmol), NaN_3 (520 mg, 8 mmol), sodium ascorbate (44.6 mg, 0.2 mmol), CuI (76 mg, 0.4 mmol), *N*,*N*′-dimethylethane-1,2-diamine (0.6 mmol) were added to degassed 5:1 DMSO/H$_2$O (10 mL).[29] The reaction mixture was stirred at RT for 1 h. The crude reaction mixture was taken up in a mixture of brine and EtOAc. The aqueous phase was extracted with EtOAc (×3). The combined organic phases were concentrated in vacuo and the residue was purified by flash chromatography over silica gel (100:1 CH_2Cl_2/methanol) to give the aryl azide **S1c** (803 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.09$ (s, 1H), 7.05 (s, 1H), 6.44 (s, 1H), 4.16 (dd, $J = 10.7$, 6.0 Hz, 1H), 4.11–4.03 (m, 1H), 3.85 (d, $J = 15.4$ Hz, 1H), 1.82 (dq, $J = 13.1$, 6.6 Hz, 1H), 1.57–1.42 (m, 1H), 1.32–1.18 (m, 1H), 0.98 (d, $J = 6.8$ Hz, 2H), 0.93 ppm (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.1$, 148.0, 141.4, 133.0, 112.7, 109.9, 109.1, 69.8, 34.3, 26.2, 16.5, 11.3 ppm; MS (EI): m/z: 206 [$M-N_3$], 219 [$M-N_2$]; elemental analysis calcd (%) for ($C_{12}H_{16}N_4O_2$): C 58.05, H 6.50, N 22.57; found: C 58.21, H 6.43, N 22.48.

Compound S1d: $CuSO_4$ (24.5 mg, 0.1 mmol) and sodium ascorbate (40 mg, 0.2 mmol) were added to a solution of **S1c** (744 mg, 3 mmol) and methyl propiolate (252 mg, 3 mmol) in ethanol/H$_2$O (2:1). The mixture was stirred at RT for 8 h. Ethanol was removed under vacuum and CH_2Cl_2 was added. The organic phase was washed with water and dried (Na_2SO_4). The residue was purified by silica gel chromatography (100:1 CH_2Cl_2/methanol) to afford **S1d** (876 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.55$ (s, 1H), 7.63 (s, 1H), 7.45 (s, 1H),

7.42 (s, 1H), 4.23 (dd, $J=10.7$, 6.0 Hz, 1H), 4.14 (dd, $J=10.7$, 6.7 Hz, 1H), 4.00 (s, 2H), 1.88 (dd, $J=13.3$, 6.7 Hz, 1H), 1.59–1.46 (m, 1H), 1.35–1.22 (m, 1H), 1.02 (d, $J=6.7$ Hz, 2H), 0.96 ppm (t, $J=7.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.6$, 161.1, 148.5, 140.6, 137.4, 133.3, 125.8, 116.5, 110.8, 110.4, 70.3, 52.5, 34.3, 26.2, 16.6, 11.4 ppm; MS (EI): m/z: 332; elemental analysis calcd (%) for ($C_{16}H_{20}N_4O_4$): C 57.82, H 6.07, N 16.86; found: C 57.55, H 6.15, N 16.73.

Compound S1e: Propiolic acid (100 mg, 1.4 mmol) and *N,N*-dicyclohexylcarbodiimide (DCC) (290 mg, 1.4 mmol) were combined in CH_2Cl_2 (10 mL), the solution was stirred for 10 min, then **S1d** (464 mg, 1.4 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg) were added. The reaction mixture was stirred for 30 min, then the precipitate was filtered off and the solvent was removed under vacuum. The residue was purified by silica gel chromatography (50:1 CH_2Cl_2/methanol) to afford **S1e** (408 mg, 76%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 8.62 (s, 1H), 8.53 (s, 1H), 8.38 (s, 1H), 8.20 (s, 1H), 4.26 (dd, $J=10.7$, 6.0 Hz, 1H), 4.18 (dd, $J=10.6$, 6.8 Hz, 1H), 4.01 (s, 2H), 3.04 (s, 1H), 1.89 (dd, $J=13.3$, 6.4 Hz, 1H), 1.59–1.46 (m, 1H), 1.28 (dd, $J=14.0$, 7.4 Hz, 1H), 1.02 (d, $J=6.7$ Hz, 2H), 0.96 ppm (t, $J=7.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=164.9$, 161.0, 157.3, 150.6, 140.7, 139.6, 136.9, 133.2, 126.0, 121.6, 117.4, 116.3, 75.6, 70.6, 52.6, 34.3, 26.2, 16.6, 11.3 ppm; MS (EI): m/z: 384; elemental analysis calcd (%) for ($C_{19}H_{20}N_4O_5$): C 59.37, H 5.24, N 14.58, found: C 59.26, H 5.12, N 14.47.

Compound S1f: $CuSO_4$ (24.5 mg, 0.1 mmol) and sodium ascorbate (40 mg, 0.2 mmol) were added to a solution of **S1e** (384 mg, 1 mmol) and **S1c** (248 mg, 1 mmol) in 2:1 ethanol/H_2O (9 mL). The mixture was stirred at RT for 8 h. Ethanol was removed under vacuum and CH_2Cl_2 was added. The organic phase was washed with water and dried (Na_2SO_4). The residue was purified by silica gel chromatography (100:1 CH_2Cl_2/methanol) to afford **S1f** (423 mg, 67%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.34$ (s, 1H), 8.77 (s, 1H), 8.66 (s, 1H), 8.27 (s, 1H), 8.22 (s, 1H), 7.67 (s, 1H), 7.46 (s, 1H), 7.38 (s, 1H), 4.33–4.11 (m, 2H), 4.02 (s, 2H), 1.90 (dt, $J=13.9$, 6.7 Hz, 1H), 1.60–1.48 (m, 1H), 1.30 (dt, $J=15.2$, 7.9 Hz, 1H), 1.03 (dd, $J=10.7$, 6.9 Hz, 3H), 1.00–0.92 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.5$, 164.9, 161.0, 158.2, 148.5, 143.2, 140.8, 139.5, 137.4, 137.1, 133.3, 126.0, 124.6, 121.3, 117.1, 116.7, 116.0, 110.6, 70.7, 70.3, 52.6, 34.4, 26.3, 16.6, 11.4 ppm; MS (MALDI-TOF): m/z: 633.4 [M+H], 665.4 [M+Na]; elemental analysis calcd (%) for ($C_{31}H_{36}N_8O_7$): C 58.85, H 5.74, N 17.71; found: C 58.69, H 5.65, N 17.53.

Compound L1: DMF (1 drop) was added to a solution of pyrene-1-carboxylic acid (148 mg, 0.6 mmol) in $SOCl_2$ (3 mL) and the mixture was stirred at 50°C for 2 h. The solvent was removed under vacuum. The residue was dissolved in dry CH_2Cl_2 (5 mL) and added dropwise to a solution of **S1f** (316 mg, 0.5 mmol) and TEA (2 mL) in dry CH_2Cl_2 (20 mL). The mixture was stirred at RT for 4 h. The solvents were removed under vacuum, the residue was dissolved in CH_2Cl_2, then washed with brine. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum then the product was purified by silica gel chromatography (CH_2Cl_2) to give **L1** (271 mg, 63%). ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta=10.95$ (s, 9H), 10.71 (s, 9H), 9.43 (s, 7H), 9.31 (s, 7H), 9.09 (s, 8H), 8.97 (s, 8H), 8.86 (s, 8H), 8.73 (d, $J=9.1$ Hz, 15H), 8.60–8.21 (m, 71H), 8.15 (t, $J=7.6$ Hz, 9H), 4.26 (dtd, $J=17.7$, 10.7, 6.8 Hz, 33H), 3.96 (d, $J=17.8$ Hz, 27H), 2.90 (d, $J=13.6$ Hz, 54H), 2.58 (s, 4H), 2.48 (s, 15H), 2.14 (s, 5H), 2.09–2.01 (m, 102H), 1.92 (d, $J=6.0$ Hz, 23H), 1.70–1.46 (m, 21H), 1.46–1.11 (m, 39H), 1.16–1.11 (m, 2H), 1.07 (d, $J=6.7$ Hz, 45H), 0.98 (t, $J=7.4$ Hz, 48H), 0.89–0.84 ppm (m, 4H); ^{13}C NMR (150 MHz, [D$_6$]acetone): $\delta=169.9$, 166.3, 162.2, 159.9, 145.2, 142.9, 141.9, 141.8, 138.7, 138.6, 134.5, 134.3, 132.8, 132.3, 132.1, 130.5, 130.3, 128.7, 128.2, 127.7, 127.6, 127.0, 126.1, 126.0, 125.9, 125.7, 122.6, 122.4, 117.6, 117.4, 71.4, 53.0, 35.9, 27.5, 17.5, 12.4 ppm; MS (MALDI-TOF): m/z: 883.9 [M+Na]; elemental analysis calcd (%) for ($C_{48}H_{44}N_8O_8$): C 66.97, H 5.15, N 13.02; found: C 66.85, H 5.24, N 13.13.

Compound S2: 3,6-Diiodo-9-octyl-9*H*-carbazole (1.06 g, 2 mmol), NaN_3 (390 mg, 6 mmol), sodium ascorbate (44.6 mg, 0.2 mmol), CuI (76 mg, 0.4 mmol), and *N,N*'-dimethylethane-1,2-diamine (0.6 mmol) were added to degassed 5:1 DMSO/H_2O (10 mL).[29] The reaction mixture was stirred at RT for 1 h. The crude reaction mixture was taken up in a mixture of brine and EtOAc. The aqueous phase was extracted with EtOAc (×1–3). The combined organic phases were concentrated in vacuo and the residue was used without further purification. $CuSO_4$ (24.5 mg, 0.1 mmol) and sodium ascorbate (40 mg, 0.2 mmol) were added to crude 3,6-diazido-9-octyl-9*H*-carbazole (650 mg, 1.8 mmol) and methyl propiolate (504 mg, 6 mmol) in 2:1 ethanol/H_2O (15 mL). The mixture was stirred at RT for 8 h. Ethanol was removed, then CH_2Cl_2 was added. The organic phase was washed with water and dried (Na_2SO_4). The residue was purified by silica gel chromatography (100:1 CH_2Cl_2/methanol) to afford **S2** (899 mg, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.61$ (s, 2H), 8.48 (d, $J=2.0$ Hz, 2H), 7.90 (dd, $J=8.8$, 2.1 Hz, 2H), 7.61 (d, $J=$ 8.8 Hz, 2H), 4.42 (t, $J=7.1$ Hz, 2H), 4.03 (s, 6H), 1.92 (q, $J=6.9$ Hz, 2H), 1.42–1.32 (m, 4H), 1.32–1.23 (m, 6H), 0.86 ppm (t, $J=6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.5$, 141.5, 129.6, 123.1, 120.4, 114.1, 110.7, 52.7, 44.1, 32.0, 29.6, 29.4, 29.3, 27.6, 22.9, 14.4 ppm; MS (MALDI-TOF): m/z: 530.4; elemental analysis calcd (%) for ($C_{28}H_{31}N_7O_4$): C 63.50, H 5.90, N 18.51; found: C 63.34, H 5.95, N 18.46.

Compound L2: 3-Aminopropan-1-ol (2 mL) was added to a solution of **S2** (530 mg, 1 mmol) in toluene (5 mL) and the mixture was heated at 80°C for 10 h. Ethyl acetate (30 mL) and H_2O (30 mL) were added and the organic phase was dried (Na_2SO_4). The solvent was removed under vacuum. The product was purified by silica gel chromatography (10:1 CH_2Cl_2/methanol) to afford **L2** (500 mg, 81.1%) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta=9.04$ (s, 2H), 8.92 (d, $J=1.7$ Hz, 2H), 8.24 (s, 2H), 8.14 (dd, $J=8.8$, 1.9 Hz, 2H), 7.91 (d, $J=8.9$ Hz, 2H), 4.62 (t, $J=7.0$ Hz, 2H), 4.11 (s, 1H), 3.65 (q, $J=5.9$ Hz, 4H), 3.57 (q, $J=$ 6.4 Hz, 4H), 2.01–1.93 (m, 2H), 1.82 (quin, $J=6.3$ Hz, 4H), 1.45 (m, 2H), 1.36 (m, 2H), 1.24 (m, 6H), 0.84 ppm (t, $J=6.6$ Hz, 3H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta=160.5$, 144.7, 141.4, 130.1, 125.5, 123.1, 120.3, 114.3, 111.8, 59.7, 37.1, 33.3, 32.1, 29.7, 29.6, 27.3, 22.9, 14.8 ppm; MS (MALDI-TOF): m/z: 616.5 [M+H], 638.5 [M+Na]; elemental analysis calcd (%) for ($C_{32}H_{41}N_9O_4$): C 62.42, H 6.71, N 20.47; found: C 62.29, H 6.76, N 20.40.

Compound S3a: $CuSO_4$ (24.5 mg, 0.1 mmol) and sodium ascorbate (40 mg, 0.2 mmol) were added to a solution of 1,3,5-tris(azidomethyl)-2,4,6-triethylbenzene[25a] (654 mg, 2 mmol) and methyl propiolate (554 mg, 6.6 mmol) in 2:1 ethanol/H_2O (15 mL). The mixture was stirred at RT for 8 h. Ethanol was removed, then CH_2Cl_2 was added. The organic phase was washed with water and dried (Na_2SO_4). The residue was purified by silica gel chromatography (100:1 CH_2Cl_2/methanol) to afford **S3a** (1.1 g, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.78$ (s, 3H), 5.71 (s, 6H), 3.93 (s, 6H), 2.76 (q, $J=8.0$ Hz, 6H), 0.96 ppm (t, $J=8.0$ Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.2$, 147.2, 140.5, 129.8, 127.1, 52.7, 48.5, 24.0, 15.7 ppm; MS (MALDI-TOF): m/z: 602.4 [M+Na]; elemental analysis calcd (%) for ($C_{27}H_{33}N_9O_6$): C 55.95, H 5.74, N 21.75; found: C 55.86, H 5.65, N 21.88.

Compound L3: 3-Aminopropan-1-ol (2 mL) was added to a solution of **S3a** (580 mg, 1 mmol) in toluene (5 mL) and the mixture was heated at 80°C for 10 h. Ethyl acetate (30 mL) and H_2O (30 mL) were added, then the organic phase was dried (Na_2SO_4). The solvent was removed under vacuum and the residue was purified by silica gel chromatography (10:1 CH_2Cl_2/methanol) to afford **L3** (637 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.52$ (t, $J=5.8$ Hz, 3H), 8.44 (s, 3H), 5.74 (s, 6H), 4.53 (t, $J=5.2$ Hz, 6H), 3.47 (dd, $J=11.5$, 5.9 Hz, 6H), 3.32 (dd, $J=$ 12.9, 6.5 Hz, 6H), 2.86 (d, $J=7.3$ Hz, 6H), 1.68 (quin, $J=6.5$ Hz, 6H), 0.77 ppm (t, $J=7.2$ Hz, 9H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta=160.6$, 147.1, 143.9, 130.7, 127.0, 59.7, 48.9, 37.1, 33.3, 24.1, 16.0 ppm; MS (MALDI-TOF): m/z: 709.6 [M+H], 731.6 [M+Na]; elemental analysis calcd (%) for ($C_{33}H_{48}N_{12}O_6$): C 55.92, H 6.83, N 23.71; found: C 55.79, H 6.75, N 23.49.

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[26] Compound **1**: ($C_{18}H_{22}N_5O_2$): $M_r = 340.41$; triclinic; space group $P\bar{1}$; $a = 9.250(3)$, $b = 10.470(3)$, $c = 10.739(3)$ Å; $\alpha = 113.007(3)$, $\beta = 100.291(4)$, $\gamma = 100.643(3)°$; $V = 904.0(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.251$ mg m^{-1-3}; $F(000) = 362$; GOF = 1.133; a total of 10117 reflections were measured in the range 3.26 to 25.0, of which 3166 were unique ($R_{int} = 0.0388$); final R indices: $R_1(I>2\sigma(I)) = 0.0706$, $wR_2 = 0.1608$. Complex **L3**·SO_4^{2-}: ($C_{63}H_{111}N_{14}O_{10}S$): $M_r = 1256.72$; monoclinic; space group $P21/c$; $a = 24.256(5)$, $b = 15.765(3)$, $c = 22.911(5)$ Å; $\alpha = 90$, $\beta = 115.15(3)$, $\gamma = 90°$; $V = 7931(3)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.053$ mg m^{-1-3}; $F(000) = 2732$; GOF = 1.133; a total of 49788 reflections were measured in the range 0.93 to 25.16, of which 14080 were unique ($R_{int} = 0.0868$); final R indices: $R_1(I>2\sigma(I)) = 0.1210$, $wR_2 = 0.3095$. CCDC-868834 and CCDC-868835 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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