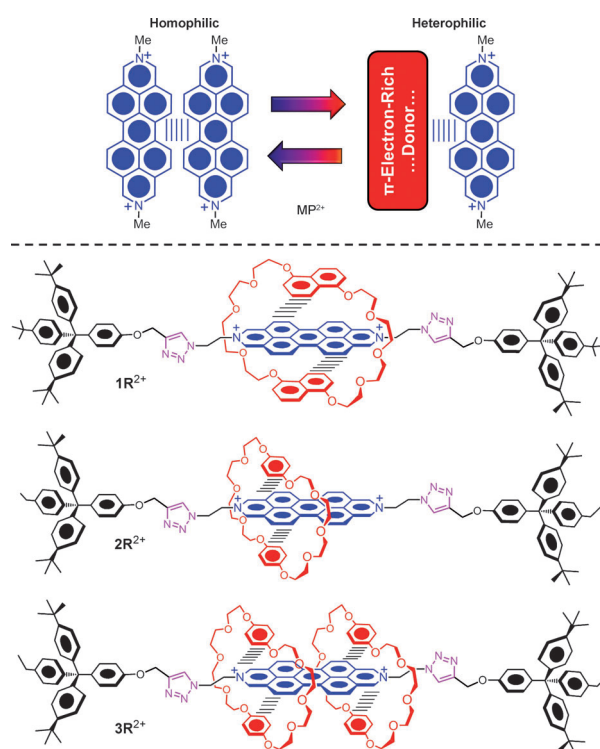


The Chameleonic Nature of Diazaperopyrenium Recognition Processes**

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Two broad classes (Scheme 1) of molecular recognition processes^[1] can be defined^[2]—namely, 1) homophilic recognition, which involves the interaction of structurally and electronically similar, if not identical, species, and 2) heterophilic recognition in which constitutionally different species come together as a result of stabilizing intermolecular non-covalent bonding interactions. Nowhere are these concepts more relevant than when considering donor–acceptor recognition processes^[3] between π -electron-rich and π -electron-deficient species. These donor–acceptor recognition motifs have aided and abetted the template-directed synthesis^[4] of mechanically interlocked molecules^[5] (MIMs), which have been employed in molecular electronic devices^[6] (MEDs) and integrated bulk systems,^[7] as well as in current state-of-the-art solar-cell technologies.^[8]

Many of these donor and acceptor units are also capable^[9] of undergoing reversible one-electron redox processes, leading to stable radical intermediates which engage^[10] in homophilic radical–radical interactions as a result of dimerization—often referred to as pimerization^[11] in the older



Scheme 1. The chameleonic nature of MP^{2+} allows for homophilic molecular recognition even as a dicationic species, as well as donor–acceptor interactions with π -electron-rich compounds. These provide an example of heterophilic recognition, which has been harnessed in the template-directed synthesis of the [2]rotaxanes $1R^{2+}$ and $2R^{2+}$ in addition to the [3]rotaxane $3R^{2+}$.

literature. Recently, we have demonstrated^[12] that these homophilic radical–radical interactions can be exploited in the template-directed synthesis^[4] of MIMs, while other researchers have shown^[13] that they can be used to fabricate organic solid-state semiconducting materials. There are very few examples of π -electronic organic molecules, however, which can exhibit both hetero- and homophilic recognition in a single redox state. This exceptional behavior, wherein the molecule can exhibit both recognition processes, analogous to that of a chameleon within its environment, is chameleonic in nature. These rare molecules have the potential to be incorporated into nanoscale architectures and functional building blocks for MIMs,^[5] MEDs,^[6] and other integrated devices.^[7,8] Herein, we report 1) the solid-state superstructure of the dimethyldiazaperopyrenium dication^[14] (MP^{2+}) based

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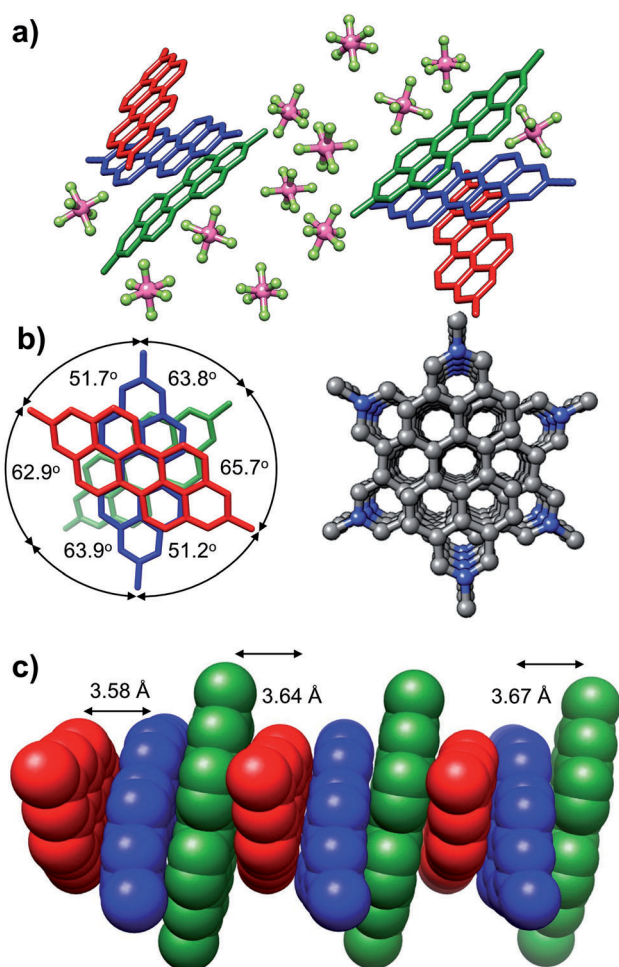


Figure 1. Solid-state (super)structures of MP-2PF₆ illustrated by the a) colored framework of MP²⁺ and ball-and-stick representation of the 12 PF₆[−] ions in one crystallographically independent cell with b) rotational stacking arrangement of the unit cell's three crystallographically independent MP²⁺ dications (red, blue, and green), and c) the space-filling representation of the continuous π stack of MP²⁺ ions. The distances between the central C–C bonds are approximately 3.6 Å, consistent with van der Waals interactions.

on the X-ray diffraction analysis^[15] of single crystals whose 2) needlelike morphology is maintained on a SiO₂ surface, as revealed by scanning electron microscopy (SEM), and whose 3) potential electronic properties were assessed by quantum mechanical calculations based on density functional theory (DFT). These homophilic characteristics of the MP²⁺ dication are accompanied by 4) their ability to serve equally well in a heterophilic capacity as π -accepting guests in their complexation with π -donating aromatic crown ether hosts, thus making it possible 5) to template the syntheses of [3]- and [2]rotaxanes by using the supramolecular assistance^[16] provided by π - π stacking and other noncovalent bonding interactions.

Orange needlelike single crystals, suitable for X-ray structural analysis,^[15] were grown by slow vapor diffusion of *i*Pr₂O into a solution of MP-2PF₆ in MeCN. The unit cell contains six MP²⁺ dications and 12PF₆[−] counterions, thus confirming the dicationic nature of the organic component in

the solid state. These six dications in the unit cell consist (Figure 1a) of two columns of three crystallographically independent MP²⁺ dications, separated by the 12 counterions and stacked one on top of the other at van der Waals distances: the two stacks are related by a crystallographic center of inversion. A closer inspection (Figure 1b) of the trio of repeating dications in the stacks reveals that, rather than their forming an in-register stack in the solid state which would maximize the degree of π -overlap of the perylene cores, albeit at significant cost to Coulombic repulsions between the pyridinium peripheries, each MP²⁺ dication is rotated by approximately 60°—the “dihedral” angles between consecutive N⁺–N⁺ vectors range from 57.2° to 65.7°—with respect to its nearest neighbors.^[17] It would appear (Figure 1c) that this packing arrangement maximizes π - π interactions^[18]—with centroid to centroid separations of 3.58, 3.64, and 3.67 Å—and minimizes Coulombic repulsions. The net result is that the entire perylene core of the MP²⁺ dication experiences overlap from its neighbors, top and bottom, with the central six-membered aromatic rings forming a continuous repeating unit while the pyridinium subunits are devoid of any face-to-face π - π stacking interactions. Although this kind of

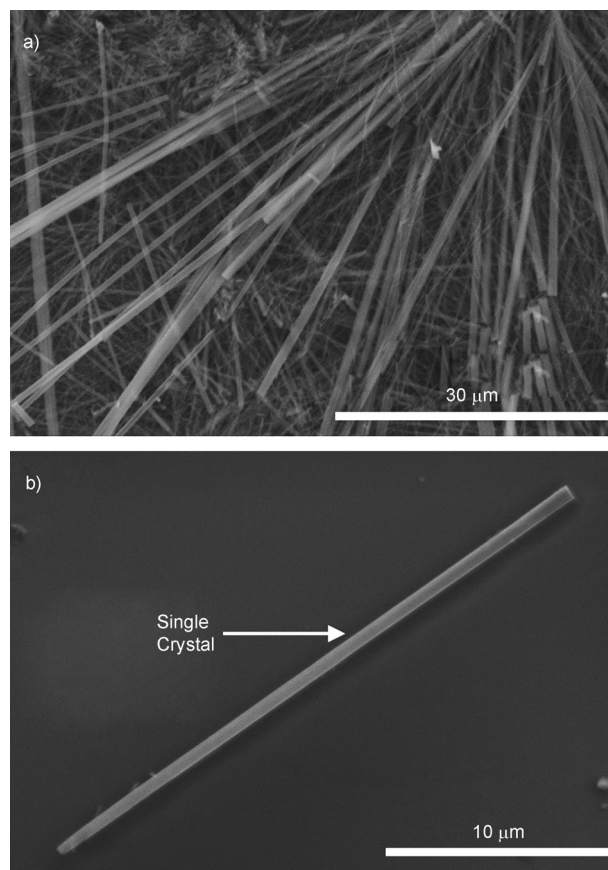


Figure 2. SEM measurements performed on crystals of MP-2PF₆ grown directly on a SiO₂ surface from MeCN using slow vapor diffusion of *i*Pr₂O at mother liquor concentrations of a) 1.2 mM, and b) 0.3 mM. At higher concentrations, thick bundles of fibers are observed, in agreement with X-ray crystallographic analysis. At lower concentrations—namely 0.3 mM—the molecules self-assemble to form single nanorods, which extend as long as 0.1 mm.

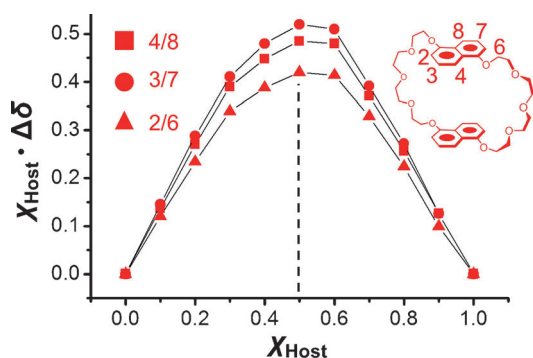


Figure 3. A Job plot between the DN38C10 host and the MP^{2+} guest obtained by plotting the $\Delta\delta$ value of the protons ($\text{H}_{2/6}$, $\text{H}_{3/7}$, $\text{H}_{4/8}$) of the DN38C10 ring observed by ^1H NMR spectroscopy (CD_3CN , 1.0 mM, 500 MHz, 298 K) against the change in the mole fraction (χ_{Host}) of the host. The plot indicates a 1:1 binding between the host and guest.

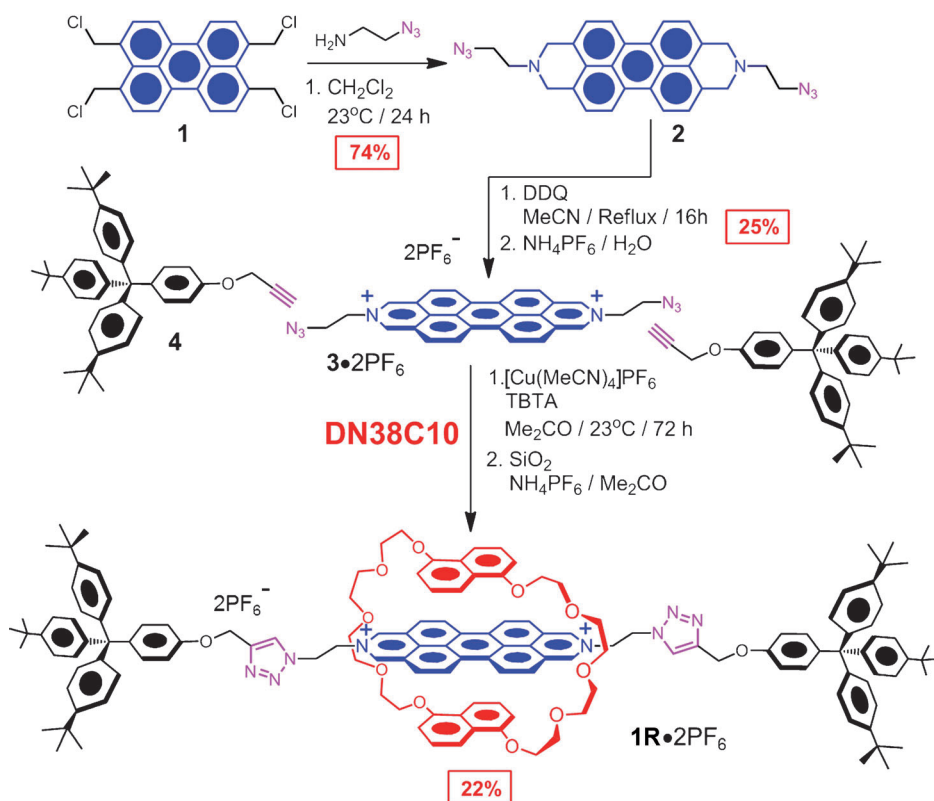
π - π stacking is relatively common for radical cations, such as the one ($\text{MV}^{\bullet+}$) obtained on reduction of methylviologen (MV^{2+}), it is rare for dications, for example, MV^{2+} , to exhibit a face-to-face homophilic stacking geometry. In the case of $\text{MP} \cdot 2\text{PF}_6$, its packing in the solid state is reflected in its morphology on a substrate such as silica, where we have found it possible, at concentrations of about 0.3 mM, to grow single crystals that display needlelike morphologies on the surface of the silica, as indicated (Figure 2) by SEM.

The high-yielding synthesis (see Experimental Section and Supporting Information) of the $\text{MP} \cdot 2\text{PF}_6$ affords us the opportunity to employ the molecular recognition of the MP^{2+} dication to template the synthesis of MIMs. Although we have reason^[12,14] to believe that this objective could be achieved through the homophilic recognition expressed by the MP^{2+} dication, we have chosen to investigate the heterophilic recognition this dication displays towards π -electron-rich macrocyclic polyethers,^[19] for example, bisparaphenylene[34]crown-10 (BPP34C10) and 1,5-dinaphtho[38]crown-10 (DN38C10). At the outset, we sought to obtain binding constants for the formation of the $\text{MP}^{2+} \cdot \text{DN38C10}$ inclusion complex by carrying out a series of isothermal titration calorimetry (ITC) experiments, having already established the existence of a 1:1 complex

from a Job Plot (Figure 3) on the basis of ^1H NMR spectroscopic measurements.^[20]

All ITC measurements were performed (see the Supporting Information) in dry, degassed MeCN at 298 K. Experiments were repeated three times, and the thermodynamic parameters reported are the calculated averages of the three runs. The results confirmed a 1:1 binding event and revealed a binding constant K_a of $1.05 \times 10^4 \text{ M}^{-1}$, which corresponds to a free energy change (ΔG) upon binding of $-5.48 \text{ kcal mol}^{-1}$. This K_a value for the $\text{MP}^{2+} \cdot \text{DN38C10}$ complex, which is over an order of magnitude higher than that for $\text{MV}^{2+} \cdot \text{DN38C10}$, is driven by a favorable change in enthalpy (ΔH) of $-8.60 \text{ kcal mol}^{-1}$, which is mediated by a negative change in entropy (ΔS) of $-10.5 \text{ cal mol}^{-1} \text{ K}^{-1}$.

We have exploited the relatively large binding constant between MP^{2+} and DN38C10 to template the syntheses of rotaxanes (Scheme 2) with both DN38C10 and BPP34C10 by employing copper-assisted azide-alkyne cycloaddition^[21–23] (CuAAC) to produce (see Experimental Section and the Supporting Information) the [2]rotaxanes **1R** $^{2+}$ and **2R** $^{2+}$, as well as a [3]rotaxane **3R** $^{2+}$ in line with the reported^[19] presence of the 1:2 complex, $\text{MP}^{2+} \cdot (\text{BPP34C10})_2$ in MeCN solution. The threading of two BPP34C10 onto a single MP^{2+} recognition site in **7** $^{2+}$ offers a rare example of a rotaxane



Scheme 2. A facile synthesis of a diazaperopyrenium derivative employed in the preparation of the [2]rotaxane **5**· 2PF_6 . The tetrachloride **1** was converted using 2-azidoethanamine into the diazide **2** which was aromatized with DDQ to give the diazidoperopyrenium salt **3**· 2PF_6 , following counterion exchange. Complexation of DN38C10 with **3** $^{2+}$ was followed by copper-catalyzed [3+2] cycloadditions to stopper the complex with propargyl ether **4** of a substituted tetraarylmethane derivative, affording **1R**· 2PF_6 in 22%, in addition to the dumbbell in 24%.

where two donor rings share one acceptor unit in the dumbbell.

The chameleonic nature of the diazaperopyrenium dication is evident from 1) its propensity, on the one hand, to aggregate with itself in solution from whence, under the appropriate conditions, it crystallizes as an extended helical-like π - π stack and 2) its ability, on the other hand, to form stable complexes with π -electron-rich aromatic crown ethers in acetonitrile solution from which it is possible to obtain rotaxanes by heterophilic templation^[12] under kinetic control.

Experimental Section

MP-2PF₆: 1,3,8,10-Tetrahydro-2,9-dimethyl-2,9-diazadibenzo[cd,lm]-perylene^[24] (100 mg, 274 mmol) was suspended at 23 °C in anhydrous MeCN (10 mL). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 249 mg, 1.10 mmol) was added as a solid, thereby resulting in an immediate color change from green to dark brown. The reaction mixture was heated under reflux for 16 h, before being cooled to 25 °C. A solution of 37% HCl (3 mL) was pipetted into the flask, whereupon precipitation occurred. The precipitate was filtered off and washed with MeCN (3 × 25 mL) and Et₂O (3 × 25 mL) to afford the dark green MP-2Cl (100 mg). Counterion exchange was performed by dissolving the dichloride salt in MeOH/H₂O (1:1) mixture, adding an excess of NH₄PF₆, and evaporating off the MeOH. The resulting precipitate was filtered and washed with an excess of H₂O to afford MP-2PF₆ (136 mg, 77%). ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C): δ = 10.21 (s, 4H), 9.99 (d, J = 9 Hz, 4H), 9.00 (d, J = 9 Hz, 4H), 5.11 ppm (s, 6H; see Figure S1 in the Supporting Information). ¹³C NMR (125 MHz, CD₃CN, 25 °C): δ = 139.1, 128.6, 128.3, 127.8, 126.0, 121.4, 49.0 ppm. HRMS (ESI) calcd for C₂₆H₁₈F₆N₂P: m/z = 503.1106 [M]⁺, found: m/z = 503.1106 [M]⁺ (see Figure S2 in the Supporting Information).

2: The tetrachloride^[25] **1** (130 mg, 58.1 mmol) was added to 2-azidoethanamine (4.99 g, 290 mmol) dissolved in CH₂Cl₂ (20 mL) and the reaction mixture was stirred at 23 °C for 48 h. The solvent was removed by evaporation under reduced pressure and the residue was suspended in H₂O, filtered, and washed with H₂O (2 × 50 mL) and Et₂O (2 × 50 mL) to afford a pure sample of the diazide **2** (102 mg, 74%) as a reddish-brown powder. ¹H NMR (500 MHz, CD₃SOCD₃, 23 °C): δ = 8.14 (d, J = 7 Hz, 4H), 7.23 (d, J = 7 Hz, 4H), 3.91 (s, 8H), 3.56 (t, J = 6 Hz, 4H), 2.80 ppm (t, J = 6 Hz, 4H). ESI-MS calcd m/z = 472.2 [M]⁺, found m/z = 472.1 [M]⁺.

3-2PF₆: The diazide **2** (101 mg, 0.213 mmol) was suspended in anhydrous MeCN (25 mL) at 23 °C, DDQ (388 mg, 1.71 mmol) was added, and the reaction mixture was heated under reflux for 16 h before being cooled to 23 °C. A solution of 37% HCl (3 mL) was pipetted into the mixture, whereupon precipitation occurred. The precipitate was filtered and washed with MeCN (3 × 25 mL) and Et₂O (3 × 25 mL) to afford (66 mg, 57%) the dark red dichloride salt of **3-2Cl**. Counterion exchange was performed by dissolving the salt in Me₂CO/H₂O (1:1), adding excess of NH₄PF₆, and evaporating off the Me₂CO. The resulting precipitate was filtered and washed with excess of H₂O to afford the crude product. Recrystallization from Me₂CO and Et₂O afforded (44 mg, 25% yield) **3-2PF₆**. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C): δ = 10.43 (s, 4H), 10.21 (d, J = 9 Hz, 4H), 9.17 (d, J = 9 Hz, 4H), 5.60 (t, J = 5 Hz, 4H), 4.58 ppm (t, J = 5 Hz, 4H) (see Figure S3 in the Supporting Information). ¹³C NMR (125 MHz, CD₃CN, 25 °C): δ = 139.0, 128.1, 126.4, 61.5, 53.6 ppm. HRMS (ESI) calcd for C₂₈H₂₀F₆N₈P: m/z = 613.1453 [M]⁺, found: m/z = 613.1447 [M]⁺.

1R-2PF₆: The stopper precursor **4** (58 mg, 0.012 mmol) and DN38C10 (37 mg, 0.058 mmol) were added to a degassed solution of the diazide **3-2PF₆** (44 mg, 0.058 mmol) in Me₂CO/CH₂Cl₂ (40 mL, 3:1). The reaction mixture was stirred for 3 h at 23 °C before

a catalytic amount of [Cu(MeCN)₄]PF₆ and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) was added. The reaction mixture was stirred for an additional 3 days at 23 °C. After evaporation of the solvents, the crude product was subjected to column chromatography (SiO₂, CH₂Cl₂/MeOH (9:1) then 1% NH₄PF₆ in Me₂CO) followed by size-exclusion chromatography on Biobeads SX-1 with CH₂Cl₂ as the eluent. 1R-2PF₆ was isolated as an orange solid (32 mg, 22%). ¹H NMR (500 MHz, CD₃CN, 25 °C): δ = 9.50 (d, 4H, J = 9 Hz), 9.32 (s, 4H), 8.50 (d, 4H, J = 9 Hz), 8.07 (s, 2H), 7.12 (d, 12H, J = 7 Hz), 7.01 (d, 4H, J = 7 Hz), 6.97 (d, 12H, J = 7 Hz), 6.81 (d, 4H, J = 7 Hz), 5.99 (d, 4H, J = 8 Hz), 5.57 (t, 4H, J = 5 Hz), 5.31 (t, 4H, J = 5 Hz), 5.22 (t, 4H, J = 8 Hz), 5.04 (s, 4H), 4.97 (d, 4H, J = 8 Hz), 4.02 (m, 8H), 3.93 (m, 8H), 3.68 (m, 8H), 3.47 (m, 8H), 1.14 ppm (s, 54H; see Figure S4 in the Supporting Information). ¹³C NMR (126 MHz, (CD₃)₂CO, 25 °C): δ = 157.5, 152.9, 152.2, 149.2, 145.4, 145.2, 140.8, 138.6, 132.9, 131.4, 130.9, 130.0, 129.3, 128.9, 126.2, 125.8, 125.1, 124.2, 123.9, 114.7, 114.3, 112.7, 103.7, 72.4, 70.7, 68.5, 63.9, 63.0, 62.2, 51.6, 50.8, 34.8, 31.7 ppm. MS (MALDI) calcd for C₁₄₄H₁₅₈F₆N₈O₁₂P: m/z = 2334.148, found: m/z = 2334.015 ([M-PF₆]⁺), HR-MS (ESI) calcd for C₁₄₄H₁₅₈N₈O₁₂ m/z = 1095.0933, m/z = 1095.0954 ([M-2PF₆]²⁺).

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