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# Syntheses and Reactions of Polycationically Substituted Azido- and Diazidobenzenes

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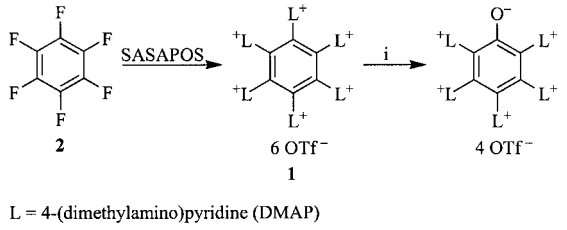
The increased reactivity of hexakis[4-(dimethylamino)-1-pyridinio]benzene hexakis(trifluoromethanesulfonate) (**1**) towards nucleophilic substitution of $DMAP^+$ ligands was used for the syntheses of the corresponding pentacationically substituted azidobenzene and the tetracationically substituted *o*-diazidobenzene. In contrast to unsubstituted azido- and diazidobenzene, the latter compounds are stable towards heat or shock. Predominantly due to the strong electrostatic effects provided by the polycationically substituted phenyl(ene) moieties, the corresponding triphenylphosphazides are stable at room temperature. Application of the Staudinger reaction yielded the corresponding polyonio-substituted aniline and *o*-phenylenediamine, respectively.



## Introduction

In previous work we have demonstrated that strong electrostatic effects present in polycationically substituted phenyl units, as first representatives of ion cluster ligands, have massive effects on a variety of chemical and physical characteristics.[1–4] Thus, the electrostatic potential of such ion cluster ligands led to low-temperature decarboxylation of a pentacationically substituted benzoic acid[2] and heteropolar C–C and C–P disconnections, induced by electrostatic stabilization of the so-formed pentacationically substituted phenyl anion.[3] Further, large bathochromic shifts of up to 140 nm (7600 $cm^{-1}$) were electrostatically induced in a variety of (azo)dyes carrying such ion cluster ligands.[4] Besides those effects, one also expects a massively increased reactivity of poly- and percationically substituted aromatics towards nucleophiles. The ease of hydrolysis of **1**, which was previously synthesized via application of the SASAPOS protocol to hexafluorobenzene (**2**),[1–4] in comparison to that of hexafluorobenzene is in line with this expectation (Scheme 1).[1]

Below we report reactions of **1** with azide ions as nucleophiles in which advantage is taken of both the increased reactivity of **1** towards nucleophiles and the electrostatically induced stabilization of azides as potentially highly reactive compounds.




Scheme 1. Hydrolysis of **1**; i) $NaHCO_3$, $H_2O$, Δ, 0.5 h, 94%.

## Results and Discussion

### Syntheses of Azido Compounds

To further exploit the enhanced reactivity of hexakis[4-(dimethylamino)-1-pyridinio]benzene hexakis(trifluoromethanesulfonate) (**1**) towards nucleophiles,[1] suspensions of **1** in acetonitrile were treated with azide ions. In this context, two different sources of azide ions were used, namely sodium azide (**3**) and *N*,*N*,*N*′,*N*′-tetramethylguanidinium azide (**4**) (Scheme 2).

All products from Scheme 2 were identified by $^1H$, $^{13}C$ NMR and IR spectroscopy, FAB-MS and elemental analyses. The structure of **6** was assumed from the appearance of exactly two signal sets for the cationic ligands. IR absorptions of the azide group are at 2133 $cm^{-1}$ (**5**) and 2146 $cm^{-1}$ (**6**) (for comparison 2134 and 2100 $cm^{-1}$ for azidobenzene,[5] 2120 $cm^{-1}$ for *o*-diazidobenzene,[6] and 2198 and 2128 $cm^{-1}$ for pentafluoroazidobenzene[7]). Depending on the reaction conditions, one or two $DMAP^+$ ligands in **1** were substituted by azide groups. With the use of sodium azide (**3**) as azide source, the number of exchanged onio ligands could be influenced by the addition of water, which decreases the nucleophilicity of the azide ions via solvation.

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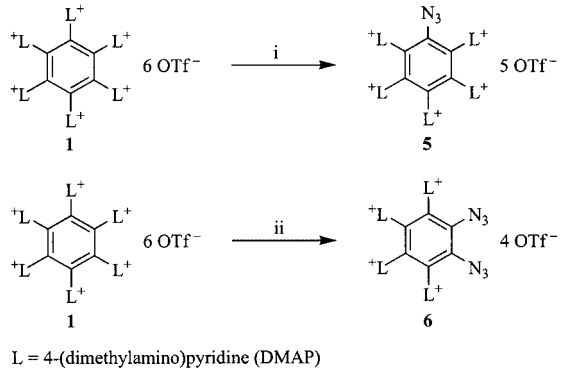



Scheme 2. Syntheses of azido compounds **5** and **6**; i) excess $NaN_3$, $H_2O$, $CH_3CN$, 3 h, 74%; alternatively **4**, $CH_3CN$, 2 h, quant.; ii) excess $NaN_3$, $CH_3CN$, 3 h, 69%; alternatively 2 equiv. of **4**, $CH_3CN$, 5 h, 86%.

When **4** was used as an azide source, the extent of onio exchange could be controlled via stoichiometry (Scheme 2). Reactions with **3** led to mixtures containing **5** (or **6**) and sodium triflate, which could not be removed easily. Hence, **4** was the preferred azide source, and was used in all further experiments.

The reaction conditions presented in Scheme 2 are in strong contrast to those needed for successful nucleophilic attack of azide ions on hexafluorobenzene (**2**). When **2** was treated with aqueous or nonaqueous solutions of sodium azide in acetone, no reactions occurred.[8] If, on the other hand, acetonitrile or dimethylformamide were used as solvents in such exchange reactions, the resulting products exploded violently during workup, presumably due to the presence of polyazido compounds.[7] Neither **5** nor **6** were explosive when heated or hit with a hammer. Thus, the results shown in Scheme 2 demonstrate the massively increased reactivity of **1** (in comparison to **2**) towards nucleophilic attack, as well as the stabilization of the azido compounds. The stability of the novel azide compounds **5** and **6** is based on the electrostatic effects of the polycationically substituted benzene units in different ways. First, a heterolytic cleavage of the N–N bond with formation of $N_2$ is energetically not favoured if a strongly electron-demanding substituent is connected to N(α). Additionally, the nitrene resulting from such bond cleavage would be destabilized by a polycationic substituent. Finally, the charge and steric demand of both the polycation and the counteranions form a high barrier for any kind of bimolecular reaction between such azide compounds as **5** and **6**. These mechanisms of electrostatic stabilization might be accompanied by the stabilizing effects of strongly increased molecular mass.

The regiochemistry in **6** is unexpected. Usually azido groups act as donor substituents and will direct a subsequent nucleophilic attack into the *m*-position. Hence, on this basis a nucleophilic attack of an azide ion towards **5** should yield a tetracationically substituted *m*-diazidobenzene derivative and not the obtained *o*-diazidobenzene derivative **6**. What are the reasons for the unexpected behaviour? The reasons are of steric nature. The approach of an azide ion towards the *o*-position of **5** attacks a $DMAP^+$ substituent which is surrounded by one other $DMAP^+$ substituent and the azido substituent. In contrast, approach of an azide ion towards the *p*- or *m*-position of **5** attacks a $DMAP^+$ substituent which is surrounded by two other $DMAP^+$ substituents. Since the azido substituent is sterically much less demanding (at least in one hemisphere of the benzene unit) than a $DMAP^+$ substituent (which may additionally be coordinated by counter anions) attack of the *o*-position will strongly be favoured, as was found in the experiments.

## Photolyses of Azido Compounds

Azidobenzene derivative **5** can be seen as an electrostatically stabilized aryl azide which is surrounded by a salt matrix consisting of five cationic ligands and their counteranions. Hence, we imagined the ion cluster nitrene **7**, generated from **5** by irradiation, might be a kinetically stable species. Consequently, a solution of **5** in acetonitrile was irradiated at 254 nm. The results are shown in Scheme 3.

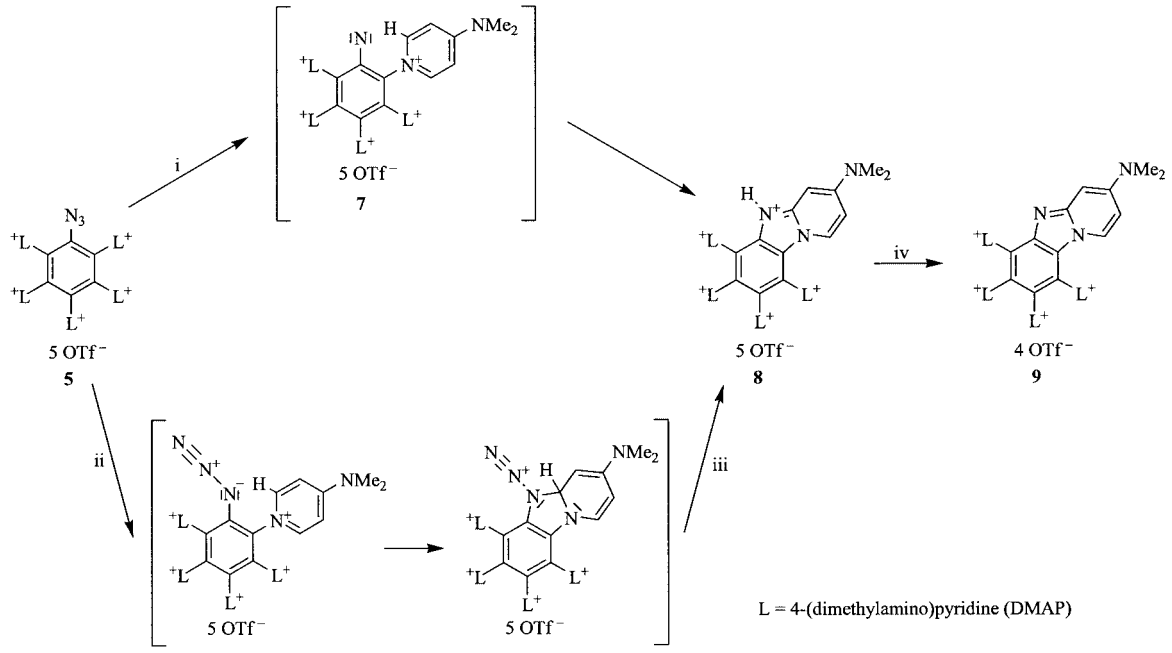
Instead of nitrene derivative **7**, the photolysis yielded the formerly unknown heterocycle **8**. After recrystallisation from water, **8** was isolated in its deprotonated form **9**, which was fully characterized by NMR, FAB-MS and elemental analysis. The IR spectrum showed no absorptions in the region of 2200–2000 $cm^{-1}$. To the best of our knowledge, this cyclisation represents a novel imidazole synthesis (cf. Scheme 3).

In accordance with the reaction mechanism found for the cyclisation of 2-azidobiphenyl under photolysis conditions,[9] we expect the formation of **8/9** to proceed via nitrene **7** as an intermediate (Scheme 3). An alternative reaction path (Scheme 3) involving nucleophilic attack of lone pair situated on the α-nitrogen of the $N_3$ function on the α-carbon centre of the neighbouring $DMAP^+$ substituent cannot be ruled out completely. However, the nucleophilicity of the α-nitrogen's lone pair (of the $N_3$ function) is massively lowered since it is connected to two strong acceptors: a diazonium function and the ion cluster ligand. Of course the α-carbon atoms of the $DMAP^+$ substituents are activated towards nucleophilic attack, but it is well known that the cationic charge of these cationic substituents is strongly delocalized via an iminium structure (via formation of a double bond between the $NMe_2$ group and the pyridine ring). Overall, the reaction path proceeding via nitrene **7** is expected to be favoured.

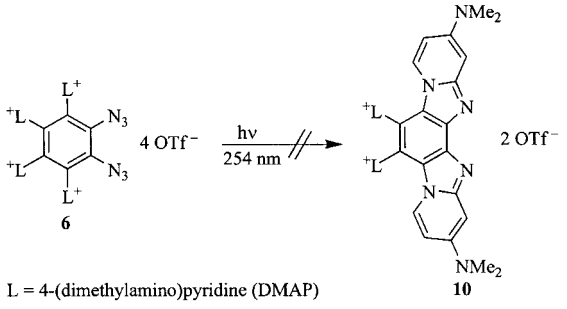
Based on the results of the photolysis of **5**, one might expect a twofold cyclisation yielding **10** if **6** is exposed to the same reaction conditions (Scheme 4).

Instead, the photolysis of a solution of **6** in acetonitrile did not yield a trace of **10**. Besides the above-shown twofold cyclisation, formation of a tetracationically substituted 1,4-dicyanobuta-1,3-diene according to the well-known ring-opening process of 1,2-diazidobenzene derivatives was

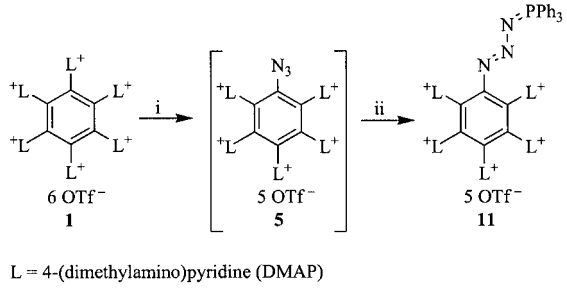
  




Scheme 3. Irradiation of **5**; i) *hν* (254 nm), $-N_2$, $CH_3CN$, 1 h; ii) *hν* (254 nm), $CH_3CN$; iii) $-N_2$, ~ 1,2-H, $CH_3CN$; iv) –HOTf, $H_2O$, Δ, 87% overall.




Scheme 4. Photolysis experiment involving **6**.




Scheme 5. Reaction sequence leading to phosphazide **11**; i) 1 equiv. **4**, $CH_3CN$, in situ; ii) $PPh_3$, $CH_3CN$, 2 h, 92% overall.

taken into account. The analytical data gave no evidence for the presence of such a compound. Only an intractable brownish tar was obtained.

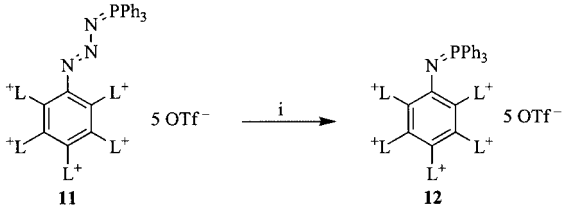
### Staudinger Reactions of Azido Compounds

The Staudinger reaction (i.e. reaction of a phosphane with an organic azide) is a widely used reaction sequence in organic chemistry. In a first step, phosphazides are formed, which are usually thermally unstable with respect to loss of nitrogen, and form iminophosphoranes (phosphazenes) at room temperature, or even below. Only a few stable derivatives are known, and all of them are sterically hindered and/or have strong electron-demanding substituents.[10–15] Both these criteria are met in **5**. In line with this, reaction of **5** (generated in situ from a suspension of **1** and guanidinium azide **4**) with triphenylphosphane led to a yellow solution of **11**, which could be isolated in pure form (cf. Scheme 5).

The isolated deeply yellow salt **11** showed no IR absorptions in the 2200–2000 $cm^{-1}$ region, indicating that no azide function was present. Phophazide **11** was fully characterized by NMR spectroscopy, FAB-MS and elemental analysis. To further explore the thermal stability of **11**, a thermogravimetric analysis was performed. When solid **11** was heated slowly, decomposition started at 34 °C and ended at 109 °C. In this temperature range loss of one mol $N_2$ is detected; further decomposition, starting at 144 °C, is not specific. Hence, refluxing a solution of **11** in acetonitrile for several hours yielded the corresponding iminophosphorane **12**, which was also fully characterized (Scheme 6).

If steric hindrance and electrostatic stabilization are reduced, the thermal stability of such phosphazides should decrease. In the *o*-diphosphazide, resulting from the reaction of **6** with 2 equiv of triphenylphosphane, the number of cationic ligands per phosphazido group is reduced from five in **11** to two. Furthermore, the steric hindrance is reduced, if one stiff $DMAP^+$ ligand is substituted by a more

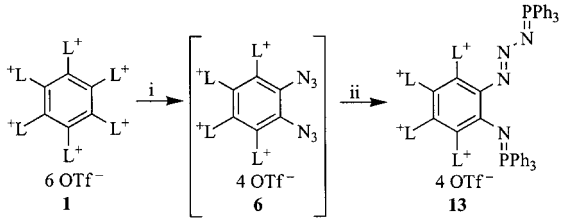
  




L = 4-(dimethylamino)pyridine (DMAP)

Scheme 6. Thermal decomposition of phosphazide **11** yielding iminophosphorane **12**; i) $CH_3CN$, Δ, 3 d, 86%.

flexible phosphazido unit. Due to this, the reaction of **6** (synthesized in situ) with triphenylphosphane yielded **13**, containing one phosphazido and one iminophosphorano group (Scheme 7).




L = 4-(dimethylamino)pyridine (DMAP)

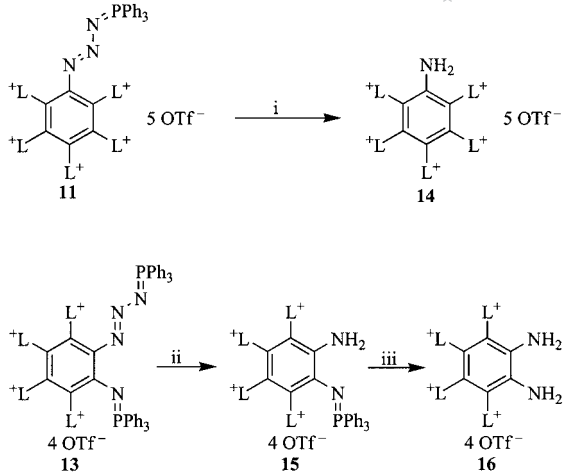
Scheme 7. Reaction sequence yielding **13**; i) +2 equiv. of **4**, $CH_3CN$, in situ; ii) $PPh_3$, $CH_3CN$, 12 h, 87% overall.

The mixed phosphazide/iminophosphorane **13** is extremely labile towards hydrolysis and thermal loss of nitrogen. Hence, $^1H$ and $^{13}C$ NMR spectra could not be interpreted unambiguously, thus **13** was characterized by FAB-MS only.

### Hydrolyses of Phosphazides and Iminophosphoranes

It is well known that hydrolysis of phosphazides and iminophosphoranes under acidic conditions yields the corresponding amino derivatives. To obtain the aniline derivative **14** derived from **5** and the *o*-phenylendiamine **16** related to **6**, solutions of compounds **11** and **13** in acetonitrile were treated with aqueous trifluoromethanesulfonic acid (Scheme 8).

Hydrolysis of **11** yielded the pentacationically substituted aniline derivative **14**. Hydrolysis of **13** at room temperature produced the amino-substituted iminophosphorane **15**; further hydrolysis in refluxing acetonitrile gave **16**. Since the reaction conditions for the solvolysis of the phosphazide group in **13** and the iminophosphorane substituent in **15** are very similar, we were not able to obtain a sample of **15** which would not contain traces of **16**. With this exception, all products from Scheme 8 were fully characterized (cf. Exp. Section).




L = 4-(dimethylamino)pyridine (DMAP)

Scheme 8. Synthesis of polyonio-substituted aniline **14** and *o*-phenylenediamine **16** derivatives via hydrolysis of phosphazides **11** and **13**; i) $H_2O/CF_3SO_3H$, $-N_2$, $-OPPh_3$, $CH_3CN$, room temp., 5 h, 97%; ii) $H_2O/CF_3SO_3H$, $-N_2$, $-OPPh_3$, $CH_3CN$, room temp., 12 h; iii) $H_2O/CF_3SO_3H$, $-OPPh_3$, $CH_3CN$, Δ (reflux), 2 d; 81% (ii+iii).

### Diazotization of the Pentacationically Substituted Aniline Derivative

Obviously it is of interest to diazotize aniline derivative **14** in order to generate an extremely electrophilic diazonium system. Therefore solutions of **14**, **11** and **12** were treated with nitrosonium tetrafluoroborate. Not unexpectedly, due to the strongly reduced nucleophilicity of the N atoms in question, this attempt met with failure. Besides the extremely low nucleophilicity, the steric hindrance in **14**, **11** and **12** could block any attack of $NO^+$. Also, there would be a huge electrostatic repulsion between the $NO^+$ cation and the pentacationic phenyl moiety as soon as they were in close proximity.

## Conclusions

As we have shown in previous work for other compound classes,[1–4] the massive electrostatic and steric effects introduced by ion cluster ligands led to a variety of unusual and unexpected reactions and properties in the chemistry of aryl azides. The hexacationically substituted benzene derivative **1** reacts under very mild conditions with azide ions to yield polyonio-substituted azido- and *o*-diazidobenzenes, which are stable towards heat and shock. The attempt to synthesize the electrostatically stabilized nitrene **7** via photolysis missed its primary target, but opened a synthetic route to the formerly unknown heterocycle **9**. Based on the electrostatic and steric effects of polycationically substituted phenyl(ene) moieties, two new isolable phosphazides were synthesized. Finally, the polyonio-substituted aniline **14** and *o*-phenylenediamine **16** were obtained for the first time via hydrolysis of the $PPh_3$ adducts of the corresponding azido compounds **5** and **6**. Since the SASAPOS protocol can not

be applied successfully to pentafluoro aniline or tetrafluoro-*o*-phenylenediamine (due to their reduced reactivity towards nucleophiles), the reaction sequence shown in Scheme 8 is the only practical way to synthesize **14** and **16**.

## Experimental Section

All reactions (except those involving water) were carried out under an $N_2$ atmosphere in dry solvents. Solvents were dried by standard methods.

**Synthesis of Pentakis[4-(dimethylamino)-1-pyridinio]azidobenzene Pentakis(trifluoromethanesulfonate) (5):** a) $NaN_3$ as the azide source: A solution of $NaN_3$ (593 mg, 9.10 mmol) in water (5 mL) was added dropwise to a suspension of **1** (1550 mg, 0.91 mmol) in acetonitrile (20 mL). After 3 h of stirring at room temperature, solid NaCl was added to the yellow solution until an organic (top) and an aqueous (bottom) phase started to form. After separation, the organic layer was evaporated to dryness and $CH_2Cl_2$ (40 mL) was added. After 12 h of stirring, the resulting precipitate was filtered, washed with $CH_2Cl_2$ (3 × 10 mL) and dried under high vacuum. Yield 987 mg (74%) of a nearly colourless powder. See below for spectroscopic data with exception of elemental analysis; the product contains ca. 10% of NaOTf. b) Guanidinium azide **4** as azide source: A solution of guanidinium azide **4** (86 mg, 0.54 mmol) in acetonitrile (2 mL) was added to a suspension of **1** (920 mg, 0.54 mmol) in acetonitrile (20 mL). The resulting yellow solution was evaporated to dryness after 2 h. After addition of $CH_2Cl_2$ (25 mL), the suspension was stirred for 1 h. The precipitate was filtered, washed with $CH_2Cl_2$ (2 × 10 mL) and dried under high vacuum to give a quantitative yield of **5** as nearly colourless powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.17 (s, 6 H, $CH_3$), 3.18 (s, 12 H, $CH_3$), 3.24 (s, 12 H, $CH_3$), 6.85 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H-3/5, *p*-DMAP), 6.86 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-3/5, DMAP), 7.02 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, H-3/5, DMAP), 7.95 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-2/6, *p*DMAP), 8.03 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-2/6, DMAP), 8.20 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, H-2/6, DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 41.42 (s, $CH_3$), 41.51 (s, $CH_3$), 110.26 (s, C-3/5, DMAP), 110.50 (s, C-3/5, DMAP), 110.60 (s, C-3/5, *p*-DMAP), 122.77 (q, $|^1J_{C,F}|$ = 320 Hz, $CF_3$), 133.78 (s, C-1/4, phenyl), 135.06 (s, C-2/3/5/6, phenyl), 139.87 (s, C-2/3/5/6, phenyl), 140.67 (s, C-2/6, DMAP), 141.10 (s, C-2/6, *p*DMAP), 141.94 (s, C-2/6, DMAP), 143.10 (s, C-1/4, phenyl), 157.42 (s, C-4, DMAP), 157.66 (s, C-4, DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1320 [M – OTf]$^+$, 1294 [M + 2H – $N_2$ – OTf]$^+$, 1142 [M – $N_2$ – HOTf – OTf]$^+$, 994 [M – $N_2$ – 3OTf]$^+$. $C_{46}H_{50}F_{15}N_{13}O_{15}S_5$ (1470.26) + 4 $H_2O$: calcd. C 35.82, H 3.79, N 11.81, S 10.39; found C 35.79, H 3.60, N 11.49, S 10.72.

**1,2,3,4-Tetrakis[4-(dimethylamino)-1-pyridinio]diazidobenzene Tetrakis(trifluoromethanesulfonate) (6). a) $NaN_3$ as Azide Source:** Solid $NaN_3$ (488 mg, 7.50 mmol) was added to a suspension of **1** (1273 mg, 0.75 mmol) in acetonitrile (20 mL). After 3 h of stirring at room temperature, water (5 mL) followed by as much solid NaCl as needed to achieve two phases, was added to the yellow suspension. After separation, the organic layer (top) was evaporated to dryness, and $CH_2Cl_2$ (30 mL) was added. After 12 h of stirring, the resulting precipitate was filtered, washed with $CH_2Cl_2$ (2 × 10 mL) and dried under high vacuum to yield 742 mg (69%) of a nearly colourless powder. See below for spectroscopic data with exception of elemental analysis; the product contains ca. 10% of NaOTf.

**b) Guanidinium Azide 4 as Azide Source:** A solution of guanidinium azide **4** (350 mg, 2.21 mmol) in acetonitrile (5 mL) was added to a suspension of **1** (1880 mg, 1.11 mmol) in acetonitrile (25 mL). The resulting yellow solution was evaporated to dryness after 5 h. After addition of $CH_2Cl_2$ (50 mL), the suspension was stirred for 3 h. The precipitate was filtered, washed with $CH_2Cl_2$ (2 × 10 mL) and dried under high vacuum to yield **5** (1182 mg, 86%) as nearly colourless powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.15 (s, 12 H, $CH_3$), 3.23 (s, 12 H, $CH_3$), 6.80 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 6.98 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 8.00 (d, $^3J_{H,H}$ = 8.3 Hz, 4 H, H-2/6, DMAP), 8.16 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-2/6, DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 41.30 (s, $CH_3$), 41.37 (s, $CH_3$), 109.98 (s, C-3/5, DMAP), 110.16 (s, C-3/5, DMAP), 121.81 (q, $|^1J_{C,F}|$ = 320 Hz, $CF_3$), 133.63 (s, phenyl), 134.25 (s, phenyl), 137.30 (s, phenyl), 141.46 (s, C-2/6, DMAP), 142.24 (s, C-2/6, DMAP), 157.39 (s, C-4, DMAP), 157.66 (s, C-4, DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1091 [M – OTf]$^+$, 1035 [M – 2$N_2$ – OTf]$^+$, 886 [M – 2$N_2$ – 2OTf]$^+$. $C_{38}H_{40}F_{11}N_{14}O_{12}S_4$ (1441.04) + 2 $H_2O$: calcd. C 35.74, H 3.47, N 15.35, S 10.04; found C 36.15, H 3.23, N 14.92, S 10.31.

**Salt 8:** A solution of **6** (800 mg, 0.56 mmol) in acetonitrile (50 mL) was irradiated by a Hg-vapour lamp (254 nm) at room temperature. After 1 h the solvent was fully removed under high vacuum, and $CH_2Cl_2$ (50 mL) was added. The resulting precipitate was filtered, washed with $CH_2Cl_2$ (2 × 10 mL) and dried under high vacuum. Recrystallisation from water yielded **8** (622 mg, 87%) as a yellow-orange powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.17 (s, 6 H, $CH_3$), 3.17 (s, 6 H, $CH_3$), 3.21 (s, 3 H, $CH_3$), 3.22 (s, 3 H, $CH_3$), 3.26 (s, 6 H, $CH_3$), 3.31 (s, 6 H, $CH_3$), 6.78 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H-3/5, DMAP), 6.80 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-3/5, DMAP), 6.90 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, H-5, attacked DMAP), 6.98 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-3/5, DMAP), 7.06 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-3/5, DMAP), 7.14 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, H-3, attacked DMAP), 7.97 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, H-6, attacked DMAP), 8.18 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-2/6, DMAP), 8.19 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-2/6, DMAP), 8.24 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-2/6, DMAP), 8.31 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-2/6, DMAP), ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 40.59 (s, $CH_3$), 41.17 (s, $CH_3$), 41.39 (s, $CH_3$), 41.58 (s, $CH_3$), 109.61 (s, C-3/5, DMAP), 109.73 (s, C-3/5, DMAP), 110.77 (s, C-3/5, DMAP), 111.02 (s, C-3/5, DMAP), 122.51 (q, $|^1J_{C,F}|$ = 319 Hz, $CF_3$), 124.98 (s, phenyl), 127.65 (s, phenyl), 129.01 (s, phenyl), 131.50 (s, phenyl), 140.18 (s, phenyl), 140.28 (s, C-2/6, DMAP), 141.98 (s, C-2/6, DMAP), 142.48 (s, C-2/6, DMAP), 143.10 (s, C-2/6, DMAP), 143.24 (s, C-2/6, DMAP), 154.17 (s, C-4, attacked DMAP), 157.36 (s, C-4, DMAP), 157.40 (s, C-4, DMAP), 157.73 (s, C-4, DMAP), 158.11 (s, C-4, DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1142 [M – OTf]$^+$, 992 [M – HOTf – OTf]$^+$, 872 [M + H – DMAP – 2OTf]$^+$. $C_{45}H_{49}F_{12}N_{11}O_{12}S_4$ (1292.17) + 3 $H_2O$: calcd. C 40.15, H 4.12, N 11.44, S 9.53; found C 40.32, H 3.97, N 11.36, S 9.74.

**Pentakis[4-(dimethylamino)-1-pyridinio]triphenylphosphazidobenzene Pentakis(trifluoromethanesulfonate) (11):** A solution of **4** (120 mg, 0.75 mmol) in acetonitrile (5 mL) was added to a suspension of **1** (1280 mg, 0.75 mmol) and triphenylphosphane (400 mg, 1.53 mmol) in acetonitrile (25 mL). The resulting yellow suspension was stirred at room temperature until its conversion to an orange solution (ca. 2 h). The solvent was fully removed under high vacuum, and the residue was suspended in $CH_2Cl_2$ (30 mL). After stirring for 5 h the precipitate was filtered, washed with $CH_2Cl_2$ (3 × 10 mL) and dried under high vacuum to yield **11** (1207 mg, 92%) as a yellow powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.07 (s, 6 H, $CH_3$), 3.13 (s, 12 H, $CH_3$), 3.14 (s, 12 H, $CH_3$), 6.51 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 6.79 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 6.80 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H-3/5, *p*-DMAP), 7.46 (dd, *J* = 12, 8 Hz, 6 H, $PPh_3$), 7.57 (dt, *J* = 8, 3 Hz, 6 H,

$PPh_3$), 7.70 (m, 3 H, $PPh_3$), 7.90 (m, 4 H, H-2/6, DMAP), 8.06 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-2/6, DMAP), 8.11 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-2/6, *p*-DMAP), ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 41.07 (s, $CH_3$), 41.30 (s, $CH_3$), 108.66 (s, C-3/5, DMAP), 110.07 (s, C-3/5, DMAP), 110.17 (s, C-3/5, *p*-DMAP), 121.86 (q, $|^1J_{C,F}|$ = 320 Hz, $CF_3$), 124.67 (d, $|^1J_{C,P}|$ = 93 Hz, C-1, phenyl), 130.54 (d, $|J_{C,P}|$ = 12 Hz, C-2/3/5/6, phenyl), 131.12 (s, $C_q$), 134.23 (d, $|J_{C,P}|$ = 11 Hz, C-2/3/5/6, phenyl), 134.83 (s, C-4, phenyl), 139.37 (s, $C_q$), 141.10 (s, C-2/6, DMAP), 141.70 (s, C-2/6, *p*-DMAP), 142.46 (s, C-2/6, DMAP), 157.10 (s, C-4, DMAP), 157.31 (s, C-4, DMAP), 157.34 (s, C-4, *p*-DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1732 [M + H]$^+$, 1583 [M + H – OTf]$^+$, 1433 [M – 2OTf]$^+$, 1320 [M – $PPh_3$ – OTf]$^+$, 1144 [M – $PPh_3$ – $N_2$ – HOTf – OTf]$^+$, 992 [M – $PPh_3$ – $N_2$ – 2HOTf – OTf]$^+$. $C_{64}H_{65}F_{15}N_{13}O_{15}P_1S_5$ (1732.55) + 1 $H_2O$: calcd. C 43.46, H 3.93, N 10.30, S 9.06; found C 43.35, H 4.02, N 10.27, S 9.31.

**Pentakis[4-(dimethylamino)-1-pyridinio]triphenyliminophosphoranobenzene Pentakis(trifluoromethanesulfonate) (12):** A solution of **11** (515 mg, 0.30 mmol) in acetonitrile (25 mL) was stirred under reflux for 3 d. During this period the intensive yellow-orange colour faded to nearly colourless. The solvent volume was reduced to ca. 5 mL under high vacuum, and diethyl ether (50 mL) was added slowly. The resulting precipitate was filtered, washed with diethyl ether (3 × 10 mL) and dried under high vacuum to yield **12** (440 mg, 86%) as a colourless powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.04 (s, 12 H, $CH_3$), 3.11 (s, 12 H, $CH_3$), 3.12 (s, 6 H, $CH_3$), 6.33 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, H-3/5, DMAP), 6.75 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-3/5, DMAP), 6.76 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-3/5, *p*-DMAP), 7.4 (m, 12 H, $PPh_3$), 7·g (m, 3 H, $PPh_3$), 7.92 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-2/6, DMAP), 8.09 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-2/6, DMAP), 8.19 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-2/6, *p*-DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 40.97 (s, $CH_3$), 41.20 (s, $CH_3$), 108.94 (s, C-3/5, DMAP), 109.85 (s, C-3/5, DMAP), 109.93 (s, C-3/5, *p*-DMAP), 121.91 (q, $|^1J_{C,F}|$ = 320 Hz, $CF_3$), 124.70 (s, C-4 onio-phenyl), 129.31 (d, $|^1J_{C,P}|$ = 108 Hz, C-1 phenyl), 130.13 (d, $|J_{C,P}|$ = 13 Hz, C-2/3/5/6, phenyl), 133.22 (d, $|J_{C,P}|$ = 11 Hz, C-2/3/5/6, phenyl), 134.13 (d, $|^4J_{CP}|$ = 3 Hz, C4 phenyl), 136.03 (d, $|^3J_{CP}|$ = 6 Hz, C2/6 onio-phenyl), 139.23 (s, C-3/5, onio-phenyl), 141.23 (s, C-2/6, DMAP), 142.26 (s, C-2/6, DMAP), 142.56 (s, C-2/6, *p*-DMAP), 148.89 (d, $|^2J_{C,P}|$ = 7 Hz, C-1, onio-phenyl), 157.11 (s, C-4, DMAP), 157.25 (s, C-4, DMAP), 157.31 (s, C-4, *p*-DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1554 [M – OTf]$^+$, 1404 [M – HOTf – OTf]$^+$, 1320 [M + H – DMAP – 2OTf]$^+$. $C_{64}H_{65}F_{15}N_{11}O_{15}P_1S_5$ (1704.53) + 2 $H_2O$: calcd. C 44.16, H 4.00, N 8.85, S 9.21; found C 43.88, H 3.97, N 8.64, S 9.50.

**2,3,4,5-Tetrakis[4-(dimethylamino)-1-pyridinio]-6-*N*-(triphenylphosphoranylidene)triphenylphosphazidobenzene Tetrakis(trifluoromethanesulfonate) (13):** A solution of **4** (346 mg, 2.19 mmol) in acetonitrile (15 mL) was added to a suspension of **1** (1859 mg, 1.09 mmol) in acetonitrile (25 mL). The suspension was stirred at room temperature until it converged into a yellow solution (ca. 1 h); this process was monitored by FAB-MS. Solid triphenylphosphane (1470 mg, 5.60 mmol) was added in one portion. Gas evolution started immediately, and the colour of the solution turned from yellow to dark orange-brown. After stirring for 12 h, the solvent was fully removed under high vacuum, $CH_2Cl_2$ (30 mL) was added, and the resulting suspension was stirred. After 3 h, the precipitate was filtered, washed with $CH_2Cl_2$ (3 × 10 mL) and dried under high vacuum to yield **13** (1641 mg, 87%) as yellow powder. FAB-MS (NBA): *m*/*z* = 1737 [M + H]$^+$, 1736 [M]$^+$, 1588 [M – OTf]$^+$, 1325 [M – $PPh_3$ – OTf]$^+$, 1147 [M – $PPh_3$ – $N_2$ – HOTf – OTf]$^+$, 997 [M – $PPh_3$ – $N_2$ – 2HOTf – OTf]$^+$.

**2,3,4,5,6-Pentakis[4-(dimethylamino)-1-pyridinio]aniline Pentakis(trifluoromethanesulfonate) (14):** A solution of trifluoromethanesulfonic acid (0.1 mL, 1.13 mmol) in water (1 mL) was added to a solution of **11** (813 mg, 0.47 mmol) in acetonitrile (25 mL). Gas evolution started immediately, and the colour of the solution changed from yellow to nearly colourless within 5 min. After stirring for additional 5 h, the solvent was fully removed under high vacuum. $CH_2Cl_2$ (30 mL) was added to the residue, and the resulting suspension was stirred for 3 h. The precipitate was filtered, washed with $CH_2Cl_2$ (3 × 10 mL) and dried under high vacuum to yield **14** (658 mg, 97%) as colourless powder. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.12 (s, 6 H, $CH_3$), 3.14 (s, 12 H, $CH_3$), 3.22 (s, 12 H, $CH_3$), 6.01 (br. s, 2 H, $NH_2$), 6.75 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-3/5, *p*-DMAP), 6.79 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-3/5, DMAP), 7.00 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-3/5, DMAP), 8.08 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, H-2/6, *p*-DMAP), 8.10 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, H-2/6, DMAP), 8.13 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, H-2/6, DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 41.22 (s, $CH_3$), 41.27 (s, $CH_3$), 109.96 (s, C-3/5, DMAP), 110.02 (s, C-3/5, *p*-DMAP), 111.03 (s, C-3/5, DMAP), 121.82 (q, $|^1J_{C,F}|$ = 320 Hz, $CF_3$), 124.29 (s, C-4, aniline), 126.74 (s, C-2/6, aniline), 139.56 (s, C-3/5, aniline), 141.08 (s, C-2/6, DMAP), 142.20 (s, C-2/6, DMAP), 142.47 (s, C-2/6, *p*-DMAP), 147.53 (s, C-1, aniline), 157.36 (s, C-4, DMAP), 158.08 (s, C-4, DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1294 [M – OTf]$^+$, 1144 [M – HOTf – OTf]$^+$, 994 [M – 2HOTf – OTf]$^+$. $C_{46}H_{52}F_{15}N_{11}O_{15}S_5$ (1444.26) + 1 $H_2O$: calcd. C 37.78, H 3.72, N 10.54, S 10.96; found C 37.50, H 3.34, N 10.88, S 10.97.

**2,3,4,5-Tetrakis[4-(dimethylamino)-1-pyridinio]-6-*N*-(triphenylphosphoranylidene)aniline Tetrakis(trifluoromethanesulfonate) (15):** A solution of trifluoromethanesulfonic acid (0.1 mL, 1.13 mmol) in water (1 mL) was added to a solution of **13** (1549 mg, 0.89 mmol) in acetonitrile (25 mL). Gas evolution started immediately, and the colour of the solution changed from yellow to nearly colourless within 5 min. After stirring overnight, the solvent was removed under high vacuum. $CH_2Cl_2$ (50 mL) was added to the residue, and the resulting suspension was stirred for 2 h. The precipitate was filtered, washed with $CH_2Cl_2$ (3 × 10 mL) and dried under high vacuum to yield **15** (972 mg) as colourless powder. FAB-MS (NBA): *m*/*z* = 1299 [M – OTf]$^+$, 1149 [M – HOTf – OTf]$^+$.

**3,4,5,6-Tetrakis[4-(dimethylamino)-1-pyridinio]-*o*-phenylenediamine Tetrakis(trifluoromethanesulfonate) (16):** A solution of trifluoromethanesulfonic acid (0.1 mL, 1.13 mmol) in water (1 mL) was added to a solution of **13** (1248 mg, 0.72 mmol) (alternatively **15**) in acetonitrile (25 mL). Gas evolution started immediately, and the colour of the solution changed from yellow to nearly colourless within 5 min. This procedure converts **13** into **15**. The solution was stirred under reflux for 2 d. Upon cooling, the solvent was removed and the residue was dried under high vacuum. After addition of acetonitrile (25 mL), a colourless precipitate remained, which was filtered, washed with acetonitrile (10 mL) and $CH_2Cl_2$ (2 × 10 mL), and dried under high vacuum to yield **16** (688 mg, 81%) as colourless powder. $^1$H NMR (400 MHz, $CD_3CN/D_2O$; 1:1): $\delta$ = 3.06 (s, 12 H, $CH_3$), 3.16 (s, 12 H, $CH_3$), 6.66 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 6.89 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-3/5, DMAP), 7.82 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-2/6, DMAP), 7.87 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H-2/6, DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN/D_2O$; 1:1): $\delta$ = 40.92 (s, $CH_3$), 40.98 (s, $CH_3$), 109.27 (s, C-3/5, DMAP), 110.21 (s, C-3/5, DMAP), 121.21 (q, $|^1J_{C,F}|$ = 319 Hz, $CF_3$), 122.54 (s, phenyl), 125.59 (s, phenyl), 137.11 (s, phenyl), 142.68 (s, C-2/6, DMAP), 143.04 (s, C-2/6, DMAP), 157.02 (s, C-4, DMAP), 157.61 (s, C-4, DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1039 [M – OTf]$^+$, 889 [M – HOTf – OTf]$^+$, 739 [M – 2HOTf – OTf]$^+$.

$C_{38}H_{44}F_{12}N_{10}O_{12}S_4$ (1189.05): calcd. C 38.39, H 3.73, N 11.78, S 10.79; found C 38.07, H 3.93, N 11.69, S 10.64.

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