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Phosphorus Complexes of the First Expanded Isophlorins

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Isophlorin (*N,N'*-dihydroporphyrin) is a reduced 20π-electron congener of porphyrin, in which the macrocyclic conjugation surrounds the carbon periphery, and does not involve the pyrrolic nitrogen atoms (Scheme 1). Isophlorin was first noted by Woodward in 1960 in connection with the synthesis of chlorophyll,[1] and since then it has been an interesting target not only as a novel porphyrinoid, but also as an nitrogen-bridged [20]annulene, serving as a key molecule at the crossroads of porphyrin and annulene chemistry.[2] However, isophlorin had been elusive for a long time because of its intrinsic propensity to undergo facile two-electron oxidation to the stable 18π-electron aromatic porphyrin. In recent years, the chemistry of isophlorins has been reactivated in light of its relevance to possible antiaromatic porphyrins.[3,4] Although analogous expanded isophlorins can also be envisaged for expanded porphyrins, which consist of more than five pyrrolic units and have been actively studied in the last two decades,[5] to the best of our knowledge no such molecule has been reported except for core-modified analogues.[6] Herein, we report the synthesis of mono- and bisphosphorus complexes of *meso*-octakis(pentafluorophenyl)-substituted octaphyrins(1.1.1.1.1.1.1.1) **1**.[7] In both cases, reversible two-electron reduction and oxidation processes have been demonstrated between 38π and 40π forms. Importantly, the latter species are the first example of expanded isophlorins that can be formulated as a [40]octaphyrin(1.1.1.1.1.1.1.1) (Scheme 1b).

As previously reported, octaphyrin **1** takes a figure-of-eight conformation with a 36π-electron network. This can be oxidized to a 34π-electron species by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or reduced to a 38π-electron species by $NaBH_4$, but its reduction to a 40π-electron annulene-like structure has never been achieved so far (Scheme 1b).[7] Encouraged by the recent report on the formation of an isophlorin analogue from N-fused porphyrin (NFP)[8] upon phosphorus complexation,[9] we examined the similar reaction of **1**. Treatment of **1** with PCl_3 (20 equiv) in the presence of triethylamine at room temperature for 24 h followed by aqueous work up and separation over a silica-gel column gave monophosphorus complex **2** and bisphosphorus complex **3** in 43 and 9% yield, respectively (Scheme 2). In the presence of an additional small amount of water and by heating at 50°C, complex **3** was obtained as the major product in 35% yield along with **2** (7%, Scheme 2). Under comparable conditions, complex **2** was converted to **3** in 47% yield.

High-resolution electrospray ionization time-of-flight mass spectrometry (ESI-TOFMS) of **2** indicated the parent positive-ion peak at $m/z = 1977.0658$ (calcd for $C_{88}H_{18}N_8F_{40}P$, $[M+H]^+$: 1977.0748). Single-crystal X-ray diffraction analysis revealed the almost C_2 symmetric figure-of-eight structure of **2**, which incorporates a phosphorus atom bound to the two pyrrolic β-carbon atoms (pyrroles A and E) and three pyrrolic nitrogen atoms (pyrroles F, G, and H) in a trigonal bipyramidal manner (Figure 1).[10a] The ^{31}P NMR spectrum exhibits a signal at $\delta = -85.59$ ppm, which is well in the range of pentacoordinated phosphorus ions with a similar coordination geometry (-50 ppm $> \delta > -100$ ppm).[11] The ^1H NMR spectrum of **2** shows seven sharp signals due to the pyrrolic β-protons and two broad signals due to the NH protons, reflecting its C_2 symmetric structure. Note that two signals due to the β protons of pyrroles A, E, and G are observed as doublets because of the magnetic coupling with the phosphorus ion, which has been confirmed by ^1H–^{31}P heteronuclear multiple bond correlation (HMBC) measurements (see the Supporting Information). The presence of the phosphorus(V) and three NH protons led to formulation of **2** as a 38π-electron species. This is consistent with the presence of a Q-like band at 1620 nm as a signature of aromatic expanded porphyrins in the UV/Vis/near infrared (UV/Vis/NIR) absorption spectrum.[5g,h] However, the ^1H NMR spectrum exhibits signals due to the pyrrolic β protons in the range $\delta = 5.13$–7.37 ppm, indicating a weak diatropic ring current effect. This can be ascribed to its twisted

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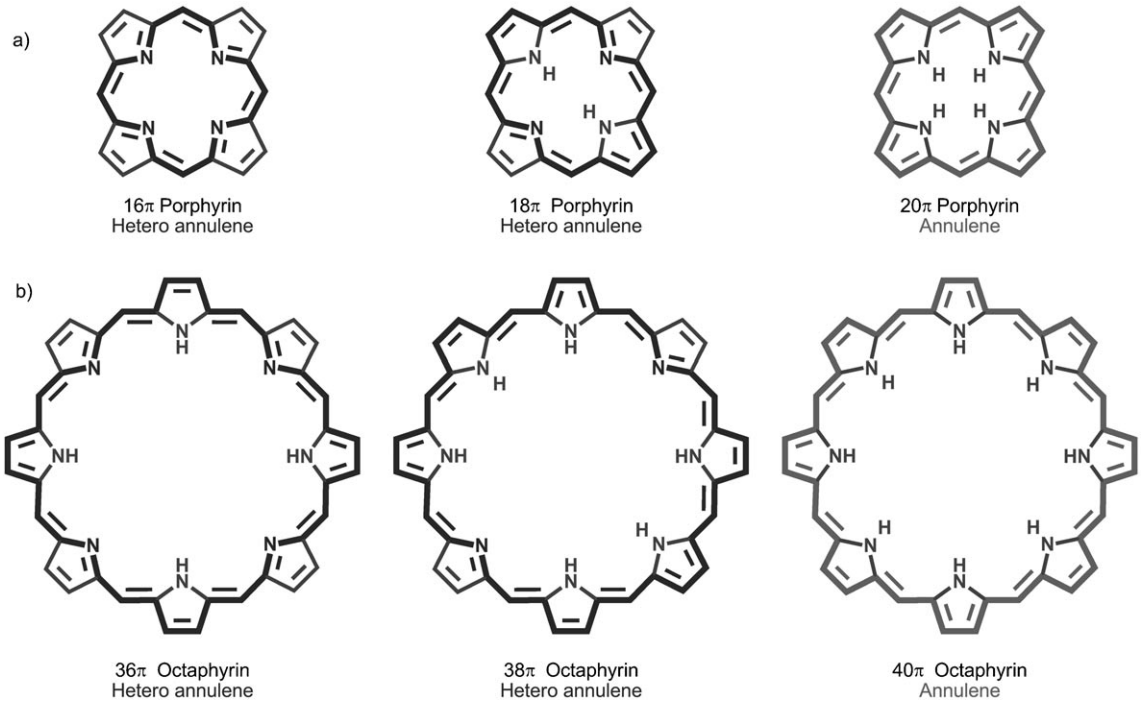
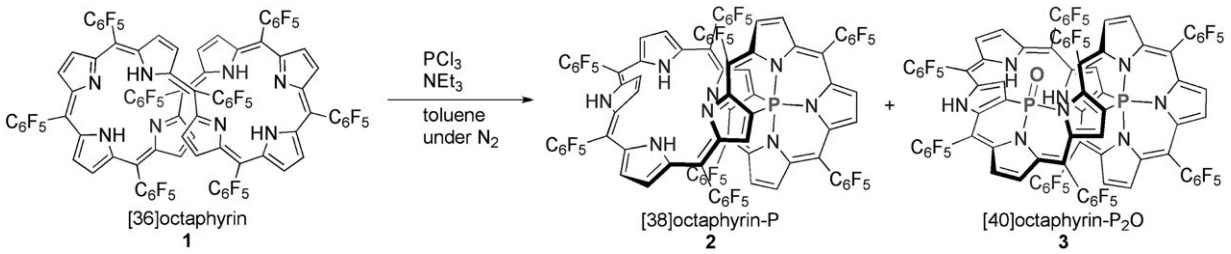


Scheme 1. Redox states of a) porphyrin and b) octaphyrin.



Scheme 2. Synthesis of octaphyrin monophosphorus(V) complex **2** and bisphosphorus(V) complex **3**.

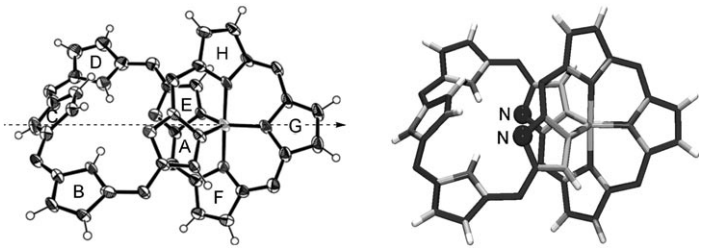
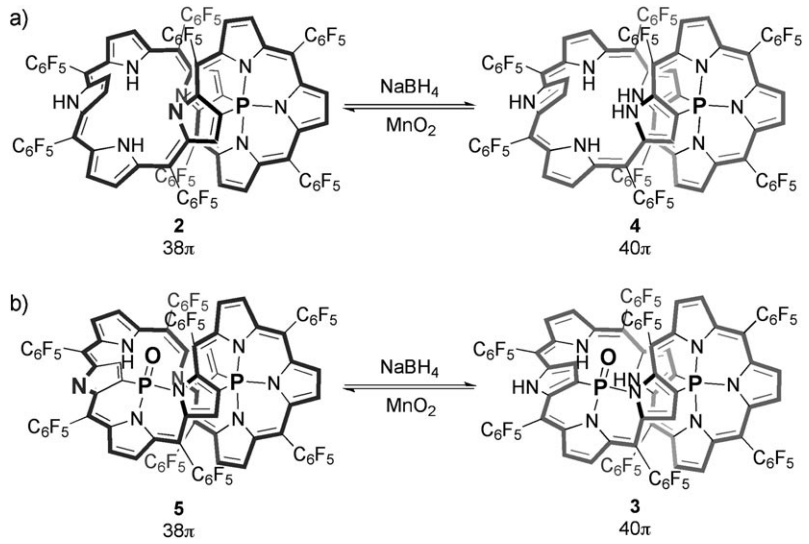


Figure 1. X-Ray crystal structure of **2** (left) and the representation of its hetero annulene circuit (right). Thermal ellipsoids represent 50% probability and *meso* aryl substituents have been omitted for clarity.

structure that does not allow for the full macrocyclic conjugation.

Interestingly, we found that reduction of **2** with $NaBH_4$ quantitatively gave **4**. Complex **4** was smoothly and quantitatively oxidized to **2** with MnO_2 (Scheme 3a). High-resolution ESI-TOFMS showed the parent negative-ion peak of **4** at $m/z = 1977.0777$ (calcd for $C_{88}H_{18}N_8F_{40}P$, $[M-H]^-$: 1977.0748), which correlates to the formulation of a 40π octaphyrin complex. The ^1H and ^{31}P NMR spectra of **4** again revealed its C_2 symmetric structure with a small ring current effect and the presence of a five-coordinate phosphorus ion. More importantly, the ^1H NMR spectrum exhibited three signals for the pyrrolic NH protons at 7.78, 7.57, and 7.47 ppm in a 2:1:2 ratio (see the Supporting Information) that supports a 40π-electron network for **4** (Scheme 1b), which corresponds to an expanded isophlorin of octaphyrin(1.1.1.1.1.1.1.1). Absence of a Q-like absorption band in the absorption spectrum of **4** is consistent with the 40π-electron state (Figure 2a).[5h] However, complex **4** is not chemically robust but undergoes facile oxidation to **2**, even when it is stored in the solid-state, probably owing to its highly reduced state.

Bisphosphorus complex **3** has been fully characterized. High-resolution ESI-TOFMS showed the parent negative-ion peak of **3** at $m/z = 2021.0206$ (calcd for $C_{88}H_{15}N_8F_{40}OP_2$, $[M-H]^-$: 2021.0211). The structure of **3** was unambiguously determined by X-ray diffraction analysis to contain two phosphorus atoms within a twisted figure-of-eight conforma-



Scheme 3. Redox interconversions of a) **2** and **4**, and b) **3** and **5**.

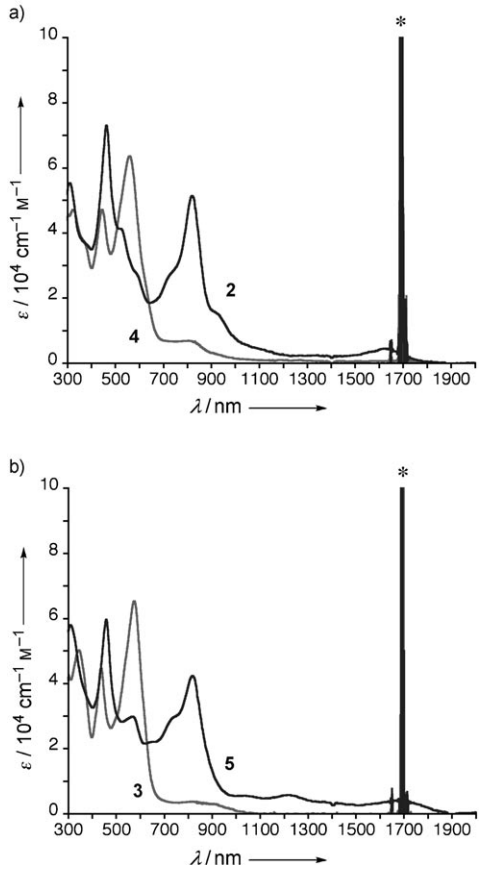


Figure 2. UV/Vis absorption spectra of a) **2** and **4**, and b) **3** and **5** in CH_2Cl_2. The background absorbance marked with * may arise from the overtones of C–H vibration of the solvent.

tion (Figure 3).[10b] One phosphorus atom takes a trigonal bipyramidal geometry similar to that of **2** and the other forms a phosphoramide bound to the nitrogen atoms of pyrroles A and B and the β-carbon atom of pyrrole C. The ^{31}P NMR spectrum of **3** showed two signals at $\delta = -104.20$ and -9.80 ppm, which were assigned to the pentacoordinate phosphorus and the phosphoramide, respectively.[9a,11] The ^{1}H NMR spectrum of **3** exhibits thirteen signals due to the β-pyrrolic protons in the range $\delta = 7.24$–6.14 ppm and three signals due to the NH protons of pyrroles C, D, and E at 7.63, 8.18, and 7.75 ppm, respectively (Figure 4a). Curiously, the NH proton in pyrrole E is split to a doublet (J(H, P) = 5.0 Hz) through coupling with the pentacoordinated phosphorus (see the Supporting Information). The presence of five P–N bonds and three NH protons leads to the formulation of **3** as a 40π-electron octaphyrin, which represents, to the best of our knowledge, the first structurally well-characterized expanded isophlorin. The absence of a Q-like band in the absorption spectrum (Figure 2b) is consistent with its 40π-electron circuit.[5h] Finally, we found that ^{18}O labeled **3** ([^{18}O]-**3**) was obtained from **1** under the reaction conditions in the presence of [^{18}O]H_2O. High-resolution ESI-TOFMS showed the parent negative-ion peak of [^{18}O]-**3** at $m/z =$ 2023.0215 (see the Supporting Information). This experiment suggests that the oxygen source of the phosphoramide in **3** is a small amount of water.

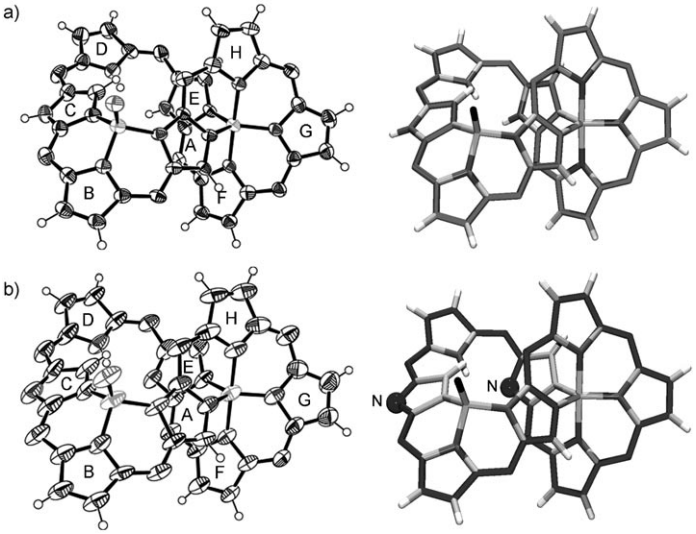


Figure 3. X-Ray crystal structures of a) **3** and the representation of its annulene circuit, and b) **5** and the representation of its hetero annulene circuit. The thermal ellipsoids represent 50% probability and *meso* aryl substituents have been omitted for clarity.

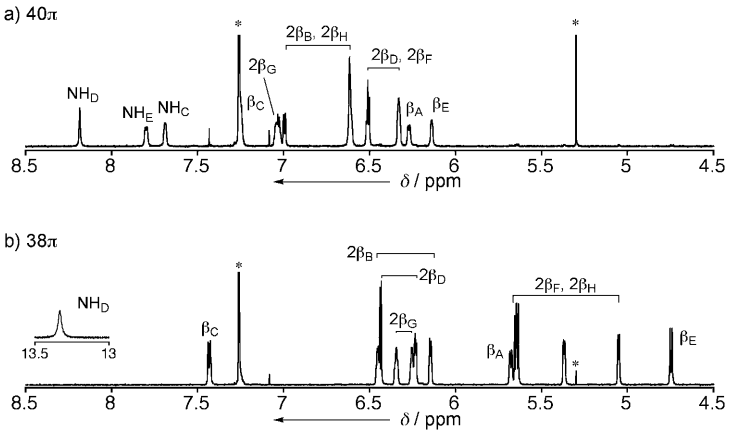


Figure 4. ^{1}H NMR spectra of a) **3** and b) **5** in $CDCl_3$ at 25 °C. The peaks marked with * are due to residual solvents and impurities.

Similar to the redox couple of **2** and **4**, the oxidation of **3** with MnO_2 quantitatively gave the [38]octaphyrin complex **5**, which was in turn reduced to **3** with $NaBH_4$. The twisted figure-of-eight structure of **5** was revealed by X-ray analysis as shown in Figure 3b. The parent positive-ion peak was observed at $m/z = 2021.0210$ (calcd for $C_{88}H_{15}N_8F_{40}OP_2$, $[M+H]^+$: 2021.0200). The ^{31}P NMR spectrum indicated signals at $\delta = -82.64$ and -4.44 ppm. The ^{1}H NMR spectrum (Figure 4b) exhibited a single signal for the NH proton at 13.33 ppm and signals due to the six β-pyrrolic protons in the range of 5.68–4.75 ppm and those due to the seven β protons in the range of 7.43–6.15 ppm, indicating a weak diatropic ring current.[12] In contrast to the facile oxidation of **4** to **2**, the complex **3** shows distinct chemical robustness and can be stored over several months in the solid state. The stability of **3** probably comes from the presence of the electron-withdrawing phosphoramide group.

Such an electron-withdrawing effect was confirmed by comparison of the cyclic voltammograms of the 38π-electron systems **2** and **5** (Figure 5). The first and second reduction potentials were observed as reversible processes at -0.66 and -1.03 V for **5**, but as irreversible processes at -0.87 and -1.35 V for **2**. The observed positive shifts upon going from **2** to **5** indicate the electron-withdrawing effects of the phosphoramide in **5**, which likely contributes to the reversibility of the reduction processes, and hence also to the enhanced stability of **5**. On the other hand, the cyclic voltammogram of **3** displays the first and second oxidation potentials at -0.14 and -0.06 V, indicating that 40π-electron system can be easily oxidized even in the presence of the phosphoramide moiety.

In summary, the mono- and bisphosphorus complexes of octaphyrin were prepared upon the treatment of **1** with PCl_3 in the presence of amine and a small amount of water. In both cases, the reversible redox interconversions between the 38π- and 40π-electron states have been demonstrated. Bisphosphorus complex **3** constitutes the first example of a structurally characterized expanded isophlorin that is stabilized by the electron-withdrawing phosphoramide moiety. Phosphorus insertion is an effective way to realize the novel electronic states of expanded porphyrins and the exploration of other phosphorus complexes of expanded porphyrins is worthy of further study.

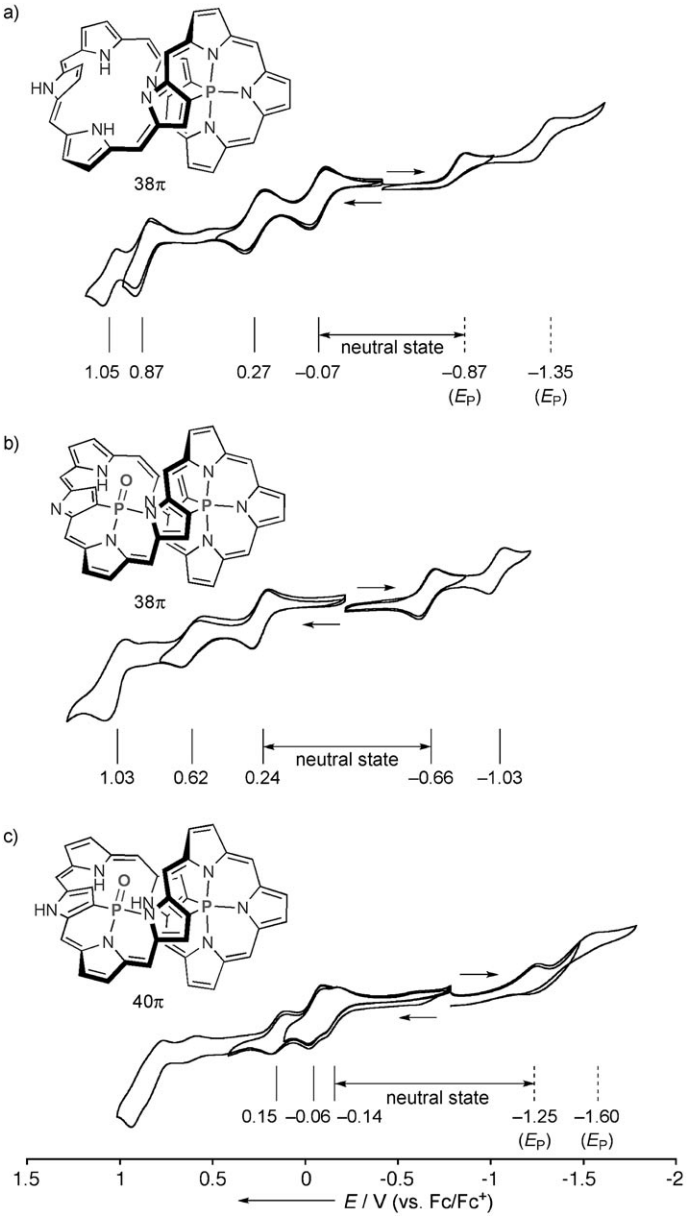


Figure 5. Cyclic voltammograms of a) **2**, b) **5**, and c) **3** in CH_2Cl_2 containing $Bu_4N^+PF_6^-$ (0.1 M) obtained at a Pt working electrode (scan rate 0.05 $V s^{-1}$) versus Fc/Fc^+.

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Keywords: aromaticity · expanded porphyrins · isophlorin · phosphorus

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[10] a) Crystallographic data for **2**: $C_{88}H_{17}F_{40}N_8P{\cdot}2(CCl_4)$ $M_r = 2284.69$; monoclinic; space group $P2_1/n$ (No.14); $a = 14.5592(14)$, $b = 21.979(2)$, $c = 30.382(3)$ Å; $\beta = 90.861(2)°$; $V = 9720.7(16)$ Å^3; $\rho_{calcd} = 1.561\ g\,cm^{-3}$; $Z = 4$; $R_1 = 0.0855$ [$I > 2.0\sigma(I)$]; $R_w = 0.2554$ (all data); GOF = 0.969; b) Crystallographic data for **3**: $C_{88}H_{16}F_{40}N_8OP_2$; $M_r = 2023.03$; monoclinic; space group $P2_1/n$ (No.14); $a = 14.239(2)$, $b = 20.995(4)$, $c = 30.676(4)$ Å; $\beta = 92.299(6)°$; $V = 9163(3)$ Å^3; $\rho_{calcd} = 1.467\ g\,cm^{-3}$; $Z = 4$; $R_1 = 0.0879$ [$I > 2.0\sigma(I)$]; $R_w = 0.2658$ (all data); GOF = 0.949; c) Crystallographic data for **5**: $C_{88}H_{14}F_{40}N_8OP_2$; $M_r = 2021.01$, monoclinic; space group $P2_1/n$ (No.14); $a = 14.099(2)$, $b = 21.669(4)$, $c = 30.284(7)$ Å; $\beta = 92.005(7)°$; $V = 9246(3)$ Å^3; $\rho_{calcd} = 1.452\ g\,cm^{-3}$; $Z = 4$; $R_1 = 0.0976$ [$I > 2.0\sigma(I)$]; $R_w = 0.3121$ (all data); GOF = 0.982. These values have been obtained by removal of the solvent molecules by using the PLATON SQUEEZE program.[13] CCDC-747644 (**2**), 747646 (**3**) and 747645 (**5**) 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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