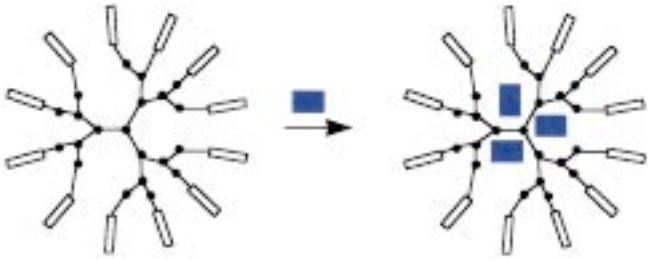

Figure 3. Schematic reprsentation of the preferential location of dye molecules in the dendrimer as the concentration of the dye is increased.

provide strong evidence for the preferential location of the guests in the interior of the dendrimer.

Experimental Section

A more extended description of the compounds, synthesis, and characterization are presented in the Supplementary Information. Moreover, experimental details and additional SAXS data are included in this section. Only a typical procedure for the synthesis of oligoethyleneoxy-modified poly(propylene imine) dendrimers is described here.

2: The pentafluorophenyl ester of 3,4,5-tris(tetraethyleneglycol)benzoic acid (8.82 g, 9.72×10^{-3} mol, 1.025 equiv per NH_2) was added to a solution of DAB-*dendr*-$(NH_2)_{16}$ (1.00 g, 5.93×10^{-4} mol) in CH_2Cl_2 (10 mL). After stirring the mixture overnight it was extracted with 0.1M NaOH and excess active ester was removed by chromatography on biobeads (BioRad, SX1) to yield pure **2** (6.28 g, 80%) as a viscous oil. Purity was confirmed by TLC (CH_2Cl_2/MeOH 95/5, $R_f = 0$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (s, 16H, NHCO), 7.16 (s, 32H, Ar-H), 4.16–4.00 (96H, Ar-OCH_2), 3.80–3.45 (672H, OCH_2), 3.42 (32H, CH_2NHCO), 3.38 (144H, OCH_3), 2.60–2.30 (84H, NCH_2), 1.80–1.40 (60H, NCH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.2$ (NHCO), 152.3 (Ar-C3,C5), 140.8 (Ar-C4), 129.7 (Ar-C1), 106.7 (Ar-C2,C6), 72.6/72.1/70.8/70.7/69.8/69.0 (OCH_2), 59.0 (OCH_3), 52.4–51.8 (NCH_2), 38.9 (CH_2NHCO), 27.5 ($NCH_2CH_2CH_2$NHCO); MALDI-TOF-MS: calcd. for $C_{632}H_{1136}N_{30}O_{256}$: 13251.9; found: 13243 $[M+H]^+$.

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Crystal Engineering of Metalloporphyrin Zeolite Analogues**

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Molecular self-assembly has emerged in recent years as an attractive approach to the fabrication of new materials.[1] This process involves the spontaneous aggregation of small molecular building blocks in solution that recognize each other through multiple molecular recognition sites to form extended architectures (while overcoming solvation forces and negative entropy effects), and it can be particularly effective in the design of nanoporous solids. However, such formula-

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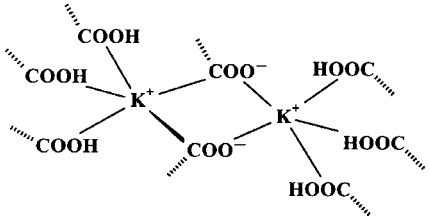
tions have enjoyed a limited success thus far, mostly as a result of the softness of the intermolecular bond, which has left open the formidable task of synthesizing stable, three-dimensional supramolecular frameworks with open voids that can be readily accessed by other species. However, a few recent successes in the construction of structurally robust porous organic crystals,[2] based on well established principles of the supramolecular design in solids[3] provide an encouraging indication that development of stable porous molecular solids with structural and functional resemblance to the naturally occurring inorganic zeolites could be feasible. The ability to organize molecular building blocks into desired supramolecular architectures through cooperative noncovalent forces requires identification of effective synthons with suitable geometries and adequate enthalpic driving forces.

In this context, several functionalized tetraarylmetalloporphyrin molecules were shown to self-assemble in different ways to yield hydrogen-bonded columns,[4] hydrogen-bonded networks with large interporphyrin voids,[5] coordination polymers propagated by coordination of the lateral substituents of a given porphyrin entity to the metal center of a similar unit,[6] and multiporphyrin arrays sustained by external transition metal centers[7] or by bidentate ligands that can bridge axially between adjacent metalloporphyrin cores.[5a, 8] Most of these materials are composed of one- or two-dimensional porphyrin aggregates, and only a small number of them yielded porous crystalline architectures.[5c, 6c, 7a] Particularly notable here is the tetra(4-carboxyphenyl)zinc porphyrin moiety [Zn^{II}(tcpp)], which was used by us in the formation of a unique, and remarkably stable, molecular sieve structure with nanosized (1.5 nm wide) channels.[5c]

Herein we report on the successful crystal engineering of a novel uniquely structured multiporphyrin assembly based on interlinked arrays of [Zn^{II}(tcpp)] and 4,4′-bipyridyl (bpy) ligands by using a simple preparative procedure, and without resorting to external transition metal auxiliaries. The crystal structure of the constructed material represents an open three-dimensional framework in which the individual metalloporphyrin units are cross-linked both axially as well as equatorially by ion-pairing interactions, metal–ligand coordination, and hydrogen bonding. Its lattice is thus fully sustained by specific intermolecular interactions, and not by virtue of van der Waals forces as is commonly observed in molecular crystals,[9] and thus provides a striking resemblance to the architecture of common zeolites.

The key feature to this successful formulation turned out to be the use of an alkali metal salt of mono-deprotonated tetracarboxylic acid, rather than of the neutral metalloporphyrin molecule. This compound allows tessellation of the commonly observed layered organization of the tcpp units not only by means of the soft hydrogen-bonding interactions,[5b,c] but also by more effective ion-pairing forces. Recent literature related to inorganic materials indicated that carboxylic derivatives may assemble as binuclear di-potassium or di-sodium (carboxyl/carboxylate)$_{6-8}$ aggregates in the presence of alkali cations,[10] but this interesting observation has not been further explored as yet in the context of deliberate synthesis of supramolecular systems. To confirm the occurrence of this synthon in the much bulkier tcpp system we initially prepared and structurally analyzed crystals of a potassium salt of [Cu^{II}(tcpp)] (**1**, see Experimental Section for detailed composition). The templating of the anionic porphyrin arrays by potassium ions leads to the formation of the binuclear {K^+_2(-COO^-)$_2$(-COOH)$_6$} unit (Figure 1). With no axial coordination to the porphyrin metal center (Cu^{II} has four-coordination preference) this structure consists of continuous columns of offset-stacked [Cu^{II}(tcpp)] species with an interporphyrin distance of 3.87 Å, which is in line with the strong tendency of the tetraphenylporphyrin units to stack in a face-parallel fashion.[11]

The characterization of the templating effect of alkali metal cations on the self-assembly of the tcpp units led to the next series of experiments in which the [Cu^{II}(tcpp)] moieties were



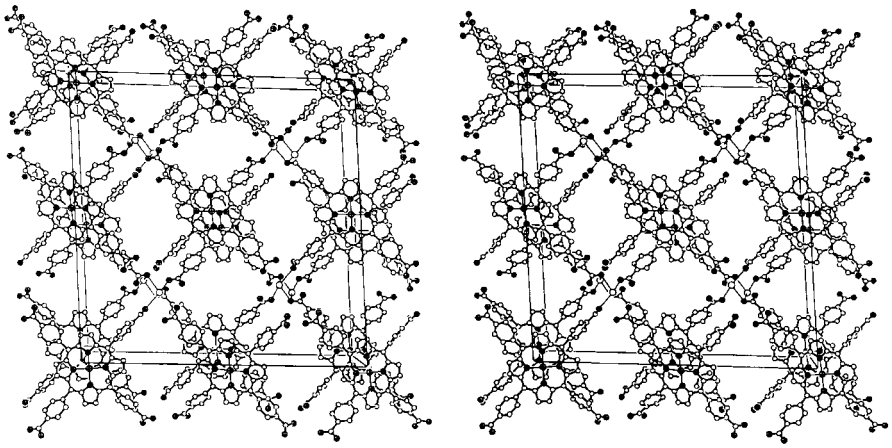


Figure 1. The structure of the binuclear {K^+_2(-COO^-)$_2$(-COOH)$_6$} unit dominant in **1** and the stereoview, approximately down the *b* axis, of its columnar crystal structure. The columns composed of stacked [Cu(tcpp)]$^-$ units are interconnected to each other through the potassium ions as well as by hydrogen bonding between the carboxylic acid groups, which yields an open architecture. Interporphyrin channels propagate along the *b* axis of the unit cell and are partly occupied by disordered nitrobenzene molecules (not shown for clarity). Every alkali metal cation is coordinated at 2.72–2.78 Å to three of the oxygen atoms (dark circles) of the carboxylic acid groups and at 2.87–3.11 Å to three other carboxylic acid groups, as well as to an additional molecule of water at 2.67 Å (not shown). The distance between the two potassium nuclei (large open circles) is 4.33 Å.

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replaced by the corresponding $[Zn^{II}(tcpp)]$ and $[Mn^{III}(tcpp)]\cdot ClO_4$ analogues, which have an added capacity to coordinate ligands in the axial, as well as the equatorial, direction. These experiments were carried out in the presence of linear bidentate ligands (for example, bpy) in an attempt to induce axial coordination between the porphyrin species, and thus extend the supramolecular interaction in three dimensions. Single crystals suitable for a detailed structural characterization could only be obtained for the zinc derivative **2** (see Experimental Section for a detailed composition) from a reaction of $[Zn^{II}(tcpp)]$ with bpy in a hot solution of methanol and ethyl benzoate in the presence of sodium chloride. Formation of the final product under such conditions is associated with proton transfer from one of the carboxy groups to the chloride anion and expulsion of hydrochloric acid. Analysis of the resulting material reveals an unprecedented zeolite-like architecture, which is perforated by wide channels in two perpendicular directions (Figure 2). This

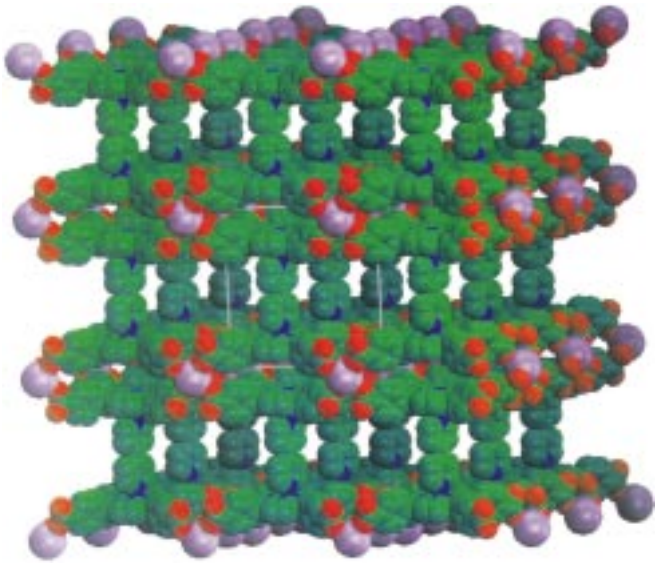

Figure 2. Space-filling (CPK) representation of the open zeolite-like supramolecular framework in **2**. It consists of sodium-tessellated metalloporphyrin bilayers extending parallel to the *ab* plane of the crystal, which are bridged by bipyridyl ligands along the *c* direction. The open galleries accessible to other molecules propagate between the bipyridyl pillars in directions parallel to the porphyrin bilayers. Na: violet, N: blue, O: red, C: green (Zn is hidden).

fascinating supramolecular assembly represents an open, single-framework three-dimensional polymer. It can be best described as composed of layers of $[Zn^{II}(tcpp)]^-$, which are held together by hydrogen bonds as well as by charge interactions and lie parallel to the *ab* plane of the crystal (Figure 3a). The sodium counter ions also provide the electrostatic force which combines two such layers back-to-back into a closely packed $[Zn^{II}(tcpp)]^-\cdot Na^+$ bilayer (Figure 3b,c). Each interaction site involves a binuclear $\{Na^+_2(\text{-}COO^-)_2(\text{-}COOH)_6\}$ unit with Na···O and Na···Na distances of 2.33–2.41 and 3.589 Å, repectively. The zinc ions, having a strong affinity for a five-coordinate environment, deviate outward (by 0.25 Å with respect to the plane of the respective porphyrin core) from the bilayer in opposite

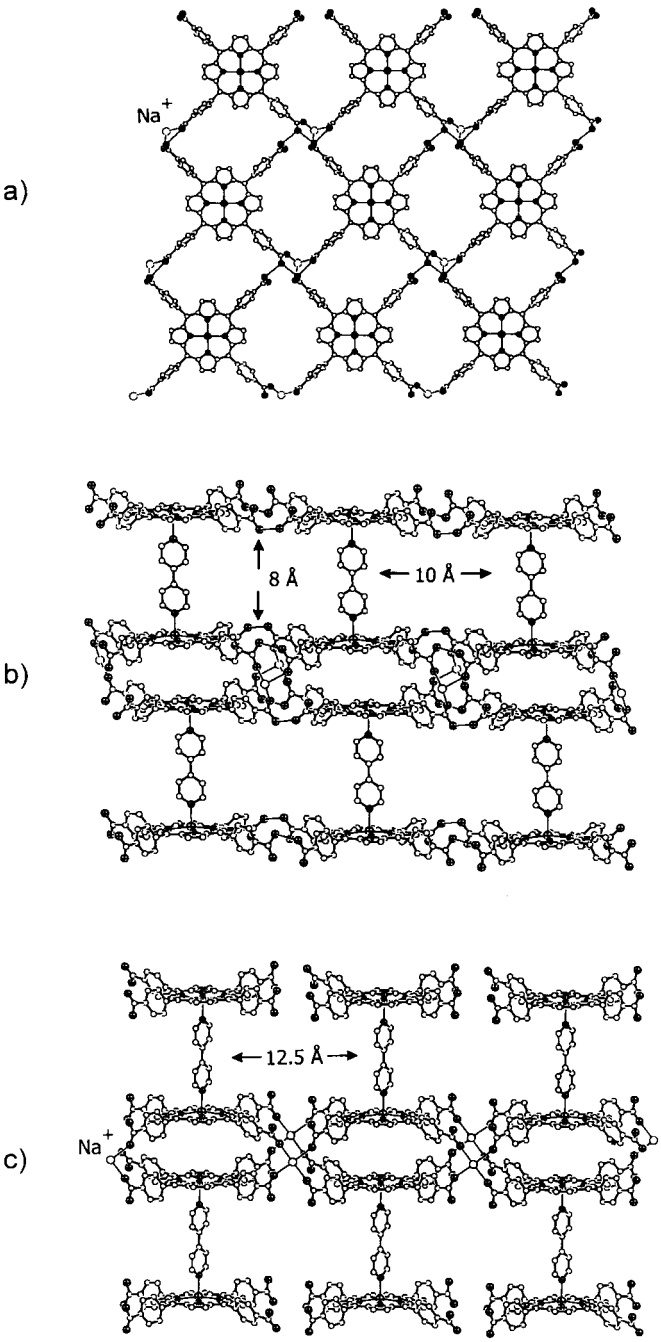

Figure 3. Detailed illustration of crystal structure **2**. a) Molecular organization in a single metalloporphyrin network, marking the hydrogen bonding (between dark circles denoting O atoms) and $Na^+\cdots O$ (Na^+ is represented by the large open circles) interactions between adjacent units. Molecules of ethyl benzoate, which protrude into the interporphyrin voids in these layers, are not shown for clarity. Sections through the crystal: b) in the *ac* plane (*a* axis is horizontal) and c) the *bc* plane (*b* axis is horizontal), illustrating the three-dimensional supramolecular coordination scheme between the constituent entities. The distances between the van der Waals surfaces of the lattice framework are indicated, which define the approximate open space available in this lattice for the intercalation of other compounds. All aromatic hydrogen atoms (not shown for clarity) were accounted for in these estimations.

directions and provide an additional binding site. This arrangement allows successively displaced bilayers to be linked together axially (the average spacing between the inner porphyrin cores of two adjacent bilayers is 11.85 Å) by the bpy

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ligands ($Zn\cdots N_{py} = 2.147$ Å) along the *c* axis of the crystal (Figure 3). The ethyl benzoate solvent is located in a disordered manner within the small interporphyrin cavities of each layer (as observed in related metalloporphyrin β-molecular networks)[5a,b] and completes the octahedral coordination sphere around each sodium cation with its carbonyl oxygen atom ($Na\cdots O(solvent) = 2.43$ Å).

The crystal lattice of this material is perforated by wide-open channels which propagate between the bpy pillars in different directions parallel to the plane of the porphyrin bilayers. The distances between the van der Waals surfaces of these pillars are rather large, approximately 10.0 Å along the *a* axis and 12.5 Å along the *b* axis, while the corresponding height of the open space is about 8 Å (Figures 2 and 3). Yet, in spite of the fact that the $[Zn^{II}(tcpp)]^- \cdot Na^+ \cdot bpy \cdot$ ethyl benzoate lattice occupies only 42% of the crystal volume (34% when the ethyl benzoate solvent coordinating to the Na^+ ions is excluded as well), the presence of no other species intercalated between the porphyrin bilayers could be identified from the diffraction data. Only very diffuse residual electron density observed in the open galleries provided evidence for their partial occupation by disordered solvent (see below). The structural refinement of this lattice alone converged at a relatively low (for such "hollow", yet crystalline systems) *R*1 value of 13.6%, which confirmed with a high degree of certainty the validity of this determination. The very loose crystal packing is also reflected in the rotational disorder of the two pyridyl rings about the main axis of the bpy molecule, as well as in the relatively large thermal displacement parameters of other atoms positioned along the channel walls. Thermogravimetric analysis (TGA/DTA) of these crystals indicated a major weight loss (32%) between 50 and 150 °C, and a more moderate and monotonic weight reduction of about 13.5% on further heating from 150 to 400 °C. Intercalation of approximately 32 volatile molecules of methanol (or a corresponding combination of methanol and water) into the crystal lattice per unit cell can be deduced from the weight loss at the first stage where there is no apparent phase transition or damage to the crystal morphology. The second part of this process is attributed to the loss of the high-boiling ethyl benzoate solvent, followed by sublimation of the bridging bpy ligands and slow decarboxylation, phase transition (at 305 °C), and conversion of the crystalline lattice to a dark amorphous powder. After subtraction of the disordered and diffused solvent contribution to the diffraction pattern, the crystallographic refinement converged with a reasonable precision at a considerably lower *R*1 value of 7.6%, without any major distortion of the supramolecular porphyrin–bipyridyl lattice being observed. The stability of this lattice, as well as its dynamic properties related to the intercalation and exchange of other compounds, are the subject of further investigations.

The supramolecular synthesis of molecular sieve materials based on effective synthons with intermolecular interaction capabilities is an exciting challenge in molecular chemistry. The ability to generate low-density, stable crystalline solids consisting of a single-framework three-dimensional lattice, in which 50% or more of the crystal volume is an open space that is accessible to other sizeable molecules provides a promising perspective for new robust molecular solids and zeolite mimics with interesting and useful properties (although such lattices are not yet sufficiently robust at high temperatures and often loose crystallinity when completely empty). Other recently developed designs of open lattices that may exhibit catalytic properties are based on the formulation of binuclear Cu_2 and Mo_2 polycarboxylate assemblies of related metalloporphyrin building blocks in which access to the porphyrin metal center is not blocked by a bridging ligand. The ordered array of open channels in this kind of structures will permit a low resistance to the diffusion of the potential reactant molecules to the active metal sites located within the channels.

Experimental Section

Tetra(4-carboxyphenyl)porphyrin was prepared by standard procedures.[12] The products were obtained by treating stoichiometric amounts of either $[Cu^{II}(tcpp)]$ and $KClO_4$ in a mixture of methanol and nitrobenzene (for **1**) or $[Zn^{II}(tcpp)]$, NaCl, and bpy (for **2**) in a mixture of methanol and ethyl benzoate (similar experiments with $[Mn^{III}(tcpp)]\cdot ClO_4$ led to crystals with very high mosaicity), followed by preparative crystallization. The diffraction data for **1** and **2** were collected on a Nonius KappaCCD diffractometer at 115 K to minimize thermal motion and evaluated by standard crystallographic techniques.

Crystal data for **1**: $\{[C_{48}H_{27}N_4O_8Cu]^- \cdot K^+ \cdot 2H_2O \cdot C_6H_5NO_2\}$, $M_r = 1049.5$, monoclinic, space group *I*2/*a* (No. 15), $a = 34.922(1)$, $b = 8.790(1)$, $c = 33.245(1)$ Å, $\beta = 93.84(1)^\circ$, $V = 10\,182.2$ Å^3, $Z = 8$, $\rho_{calcd} = 1.369$ g cm^{-3}, $2\theta_{max} = 51.5^\circ$, 9391 unique reflections. Final $R1 = 0.119$ for 5684 reflections with $F > 4\sigma(F)$, $R1 = 0.189$, $wR2 = 0.328$, and GOF = 1.007 for all data, with the nitrobenzene and one molecule of water being severely disordered in the lattice (the nitrobenzene exhibits a twofold orientational disorder about the normal to its plane). When the contribution of the disordered solvent (located in the voids of the interporphyrin channel of the lattice) to the diffraction pattern is subtracted from the observed data by the "Squeeze" method,[13] the final $R1 = 0.079$ for 5428 reflections with $F > 4\sigma(F)$, $R1 = 0.144$, $wR2 = 0.206$, and GOF = 1.051 for all data.

Crystal data for **2**: $\{[C_{48}H_{27}N_4O_8Zn]^- \cdot Na^+ \cdot \frac{1}{2}(C_{10}H_8N_2) \cdot C_9H_{10}O_2 \cdot (CH_3OH)_x\}$, triclinic, space group $P\bar{1}$ (No. 2—based on intensity statistics), $a = 16.315(1)$, $b = 17.405(1)$, $c = 18.410(1)$ Å, $\alpha = 89.59(1)$, $\beta = 84.33(1)$, $\gamma = 82.52(1)^\circ$, $V = 5157.8$ Å^3, $Z = 2$, $2\theta_{max} = 51.3^\circ$, 19 005 unique reflections. For $x = 16$ (based on TGA), $M_r = 1617.0$, $\rho_{calcd} = 1.041$ g cm^{-3}, $\rho_{meas.} \approx 1.0$ g cm^{-3}. This crystallographic refinement (excluding the lattice-diffused methanol solvent) converged at $R1 = 0.136$ for 15037 reflections with $F > 4\sigma(F)$, $R1 = 0.161$, and $wR2 = 0.380$ for all data. After subtracting the contribution of all disordered solvent (ethyl benzoate as well as methanol) to the diffraction pattern from the observed data by "Squeeze",[13] the final $R1 = 0.076$ for 14 500 reflections with $F > 4\sigma(F)$, $R1 = 0.093$, $wR2 = 0.231$, and GoF = 1.100 for all data; values of min/max residual electron density: 0.89/ − 0.63 e Å^{-3}. This crystal structure was also analyzed in the space group *P*1 to ensure that the apparent structural disorder is not an artifact of selecting a wrong space group. This analysis revealed similar disorder features in the structural model and high correlation coefficients between equivalent atomic parameters. In all the calculations the hydrogen atoms attached to carbon atoms were placed in calculated positions and added as fixed contributions to the structure factors. Different distributions of the carbon–oxygen bond lengths provided a clear discrimination between the carboxylic and carboxylate groups in the tcpp moieties.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137545 and -137546. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Charge Separation in a Molecular Triad Consisting of an Iridium(III) – bis-terpy Central Core and Porphyrins as Terminal Electron Donor and Acceptor Groups**

Isabelle M. Dixon, Jean-Paul Collin,* Jean-Pierre Sauvage,* Francesco Barigelletti, and Lucia Flamigni*

Synthetic multiporphyrin systems represent interesting mimics of the natural photosynthetic reaction centers in green plants[1a] and bacteria.[1b] In photosynthetic bacteria, one of the key reactions is electron transfer from the singlet excited state of the primary donor (special pair of bacteriochlorophylls, P) to a tetrapyrrolic unit (accessory bacteriochlorophyll, B), which is followed by another ultrafast electron transfer to a secondary acceptor (bacteriopheophytin, H). This three-component natural device (triad) is extremely efficient and has triggered the synthesis and study of many triads, designed to function in a similar way.[2]

Until now most of these systems relied on covalent bonds. Recently, alternative strategies were proposed for constructing multiporphyrin assemblies, mostly based on hydrogen bonds,[3a] mechanical bonds,[3b] or coordination bonds.[3c] In particular, ruthenium(II) bis-terpy (terpy = 2,2′:6′,2″-terpyridine) has been used as a central complex[4] that 1) gathers together the various electro- and photoactive groups to be incorporated in the triad, and 2) provides a central electroactive species that participates in the multistep electron-transfer process. This latter function can be complicated by energy-transfer processes, due to the presence of a relatively low lying (ca. 1.9 eV) triplet metal-to-ligand charge transfer (^{3}MLCT) state located on the $[Ru(terpy)_2]^{2+}$ core.[5] To circumvent these potential difficulties we looked for an alternative metal, and iridium(III) appeared to be particularly well suited. The $[Ir(terpy)_2]^{3+}$ unit forms the central complex (A_1) of the present triad (Scheme 1), in which a free-base porphyrin (PH_2) is the primary electron donor (D), and a gold(III) porphyrin (PAu) the secondary electron acceptor (A_2). In the natural photosynthetic reaction center, D, A_1, and A_2 are P, B, and H, respectively. It is noteworthy that the three-component assembly PH_2-[Ir]-PAu ($\mathbf{5}^{4+}$) has a linear arrangement with very little flexibility and hence good control over the geometry of the ensemble. Given the properties of

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