

Metal-Mediated Self-Assembly of Molecular Squares of Porphyrins Rimmed with Coordination Compounds

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Partially coordinated *meso*-tetra(4'-pyridyl)porphyrin, in which two out of four peripheral 4'-(N)py sites are bound to inert Ru^{II} complexes, self assembles with cationic square-planar Pd^{II} or neutral octahedral Ru^{II} 90° angular units to

yield a new family of molecular squares, in which the periphery of the porphyrins is rimmed with coordination compounds.

Introduction

The metal-mediated self-assembly of bi- and polydentate *N*-donor ligands is a widely used approach to the efficient construction of discrete two- and three dimensional supramolecular architectures.^[1] The same self-assembly principle has been applied to the construction of multiporphyrin assemblies^[2] which can either mimic naturally occurring multichromophore aggregates, such as the photosynthetic reaction center and the light harvesting complex of purple bacteria,^[3] or can be used as electron- and/or energy-transfer molecular devices for advanced technological tasks.^[1a,2] In such supramolecular architectures the position and relative orientation of the chromophores is essentially dictated by the nature and geometry of the metal auxiliaries.^[4] In particular, there has been substantial recent interest in the construction of cyclic multiporphyrin assemblies (molecular squares) which lock the chromophores in a mutually coplanar geometry.^[1a,5]

In general, the relatively few examples of molecular squares of porphyrins based on homonuclear metal corners or edges have been prepared by coordination of *meso*-di(4'-pyridyl)porphyrins *basic* building blocks,^[6] either *cis* (90° angular, *A_b*) or *trans* (180° linear, *L_b*), with suitable coordination compounds, precursors for angular (90°, *A_a*) or linear (180°, *L_a*) *acidic* building blocks.^[7,8] Recently, we described an efficient approach to heterobimetallic cyclic porphyrin assemblies featuring different diagonally opposed metal ions.^[9]

Here we report the stepwise construction of a new class of molecular squares of porphyrins comprising two types of metal centers: the nuclei of one metal have a structural

role (corners of the square, either Pd or Ru), while those of the other metal (Ru) rim the periphery of the chromophores.

Results and Discussion

In the first step of this synthetic approach two out of four peripheral 4'-(N)py sites of 4'-TPyP^[6] were coordinated to metal centers. We reported that treatment of *meso*-(4'-pyridyl)porphyrins with the Ru^{II} complex *cis,fac*-[RuCl₂(DMSO)₃(CO)] (**1**) leads to the selective coordination of *cis,cis,cis*-[RuCl₂(DMSO-S)₂(CO)] fragments ([Ru]) to the peripheral basic sites of the chromophores.^[10] The 4'-(N)py–[Ru] bonds are both stable and inert. Thus, reaction of 4'-TPyP with two equivalents of **1** yielded a mixture of the five possible adducts (plus unchanged 4'-TPyP):^[11] the two bis-ruthenated isomeric products, *cis*-4'-TPyP([Ru])₂ (**2**) and *trans*-4'-TPyP([Ru])₂ (**3**), were obtained in pure form by chromatography. The nature and geometry of **2** and **3** were unambiguously established from a combination of ¹H NMR spectroscopy (Figure 1) and mass spectrometry. The number of NMR signals for the eight pyrrole protons (β-H) proved to be particularly important in distinguishing between the *cis* and *trans* isomers, since the other resonances are only marginally different: *trans*-4'-TPyP([Ru])₂ (**3**) gives two doublets of the same intensity (4β-H each), while *cis*-4'-TPyP([Ru])₂ (**2**) shows two doublets plus two singlets of the same intensity (2β-H each).

The sulfoxide resonances (four equally intense singlets in the region for *S*-bonded DMSO which may overlap partially or completely in pairs) confirm through integration that two [Ru] fragments are bound to each 4'-TPyP and are always consistent with the *cis,cis,cis* geometry of each ruthenium unit.^[13] Electrospray mass spectrometry (ES-MS) analysis of **2** and **3** gave peaks corresponding to MH⁺ (*m/z* = 1332.0, calculated 1332.2) and MH₂²⁺ (*m/z* = 667.4, calculated 666.6), plus fragmentation peaks deriving from the loss of one or both [Ru] units; the isotopic distribution

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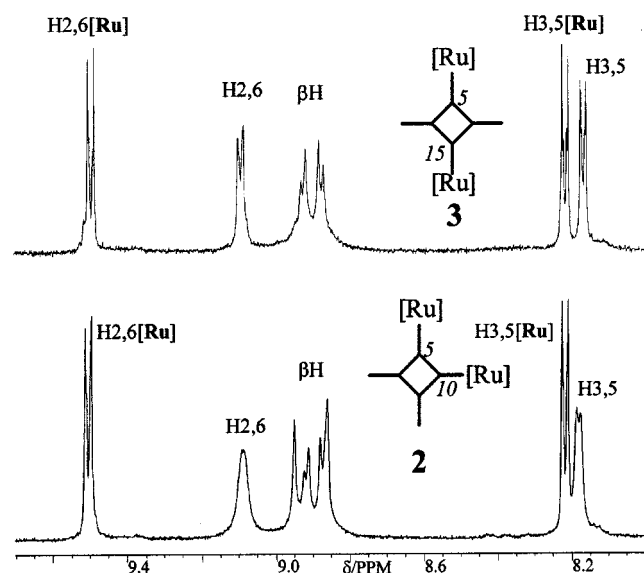


Figure 1. Downfield region of the ^1H NMR spectrum of *cis*-4'-TPyP([Ru]) $_2$ (2)^[12] (bottom) and *trans*-4'-TPyP([Ru]) $_2$ (3) (top) with the corresponding schematic building block representations; see Figure 2 for labeling scheme; [Ru] = *cis,cis,cis*-[RuCl $_2$ (DMSO-*S*) $_2$ (CO)]

patterns were also consistent with the calculated isotopic envelope expected for such isomers.

We demonstrated that coordination of one (or more) [Ru] unit(s) to 4'-PyPs^[6] does not affect significantly the further reactivity of the uncoordinated 4'-(N)py ring(s).^[11] Compounds 2 and 3, with two residual unbound 4'-(N)py rings either at 90° or 180°, are thus described as A_b and L_b building blocks, respectively, and are suitable for the construction of molecular squares. As examples, we investigated the reactivity of 2 towards [Pd(dppp)(OTf) $_2$] (4) [dppp = 1,3-bis(diphenylphosphanyl)propane, OTf = triflate] and *trans*-[Ru II Cl $_2$ (DMSO-*S*) $_4$] (5), which are precursors for the double-charged square-planar [Pd(dppp)] $^{2+}$,^[7,8] and for the neutral octahedral *trans,cis*-[RuCl $_2$ (DMSO-*S*) $_2$] (*rRu*) A_a units,^[9–11] respectively. The reaction of 2 with 4 or 5 was monitored by ^1H NMR spectroscopy in CDCl $_3$ solution, which established that titration of 4 into a CDCl $_3$ solution of 2 led readily to the quantitative formation of [Pd(dppp){*cis*-4'-TPyP([Ru]) $_2$ }] $_2$ (OTf) $_4$ (6) (Figure 2).

Complex 6 is an example of a new type of heterobimetallic [2+2] molecular square of porphyrins in which the Pd II ions form two corners of the square, while the four Ru II complexes rim the outside of the assembly. Integration of the NMR resonances confirmed the 2:1:1 ratio between [Ru], 4'-TPyP, and dppp expected for 6. ES-MS analysis of 6 gave an [M – 3OTf] peak of m/z = 1240.0 (calculated 1240.3) resulting from a loss of three triflate anions from a total of four (and also a series of fragmentation peaks corresponding to the loss of [Ru] units and neutral ligands). Coordination of the Pd–bisphosphane fragment to 2 induced characteristic shifts of NMR signals; these included mainly the ^1H NMR resonances of the previously unbound 4'-(N)py rings (Figure 3) and the proton-decoupled ^{31}P NMR signal (upfield shift of ca 10 ppm relative to 4, as is

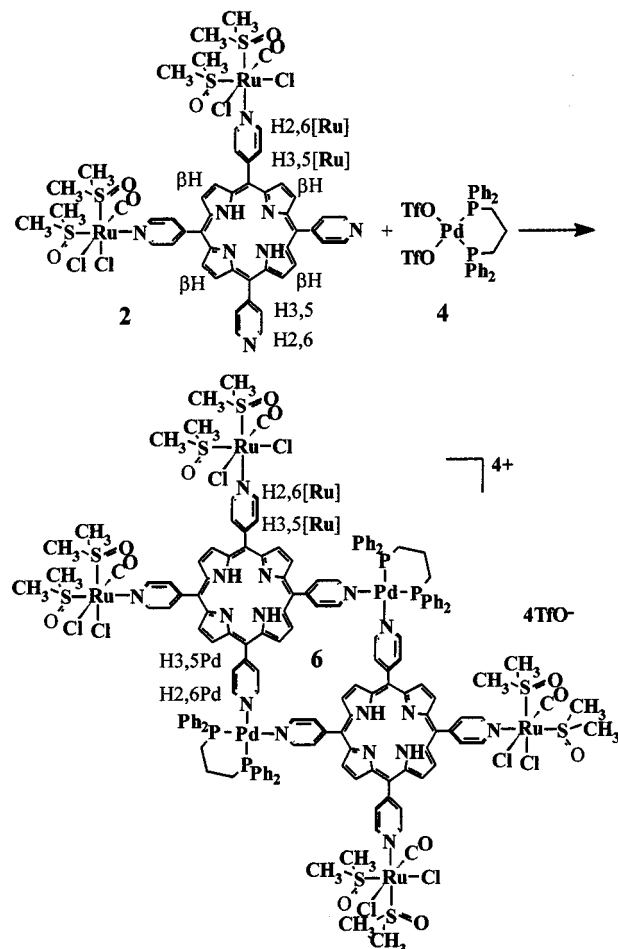


Figure 2. Schematic synthesis of [Pd(dppp){*cis*-4'-TPyP([Ru]) $_2$ }] $_2$ (OTf) $_4$ (6) with labeling scheme

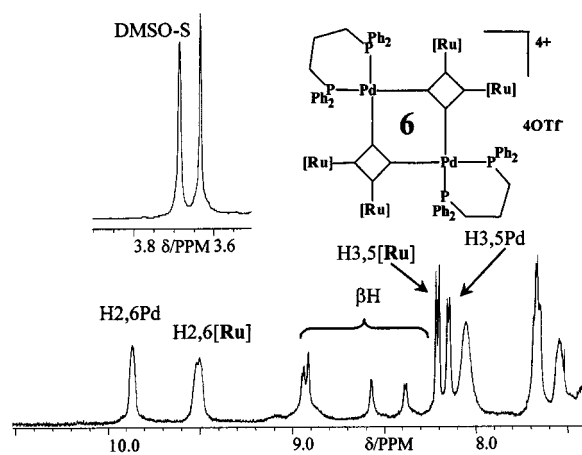


Figure 3. Downfield region, and DMSO-*S* region (insert), of the ^1H NMR spectrum of [Pd(dppp){*cis*-4'-TPyP([Ru]) $_2$ }] $_2$ (OTf) $_4$ (6) with its schematic representation; see Figure 2 for labeling scheme

the case in similar compounds^[7,9]). In 6 the resonances of the 4'-(N)py–Pd rings are well resolved from those of the 4'-(N)py–[Ru] rings, which were almost unshifted upon formation of the square. The most downfield H2,6 and the most upfield H3,5 signals (correlated in the COSY spec-

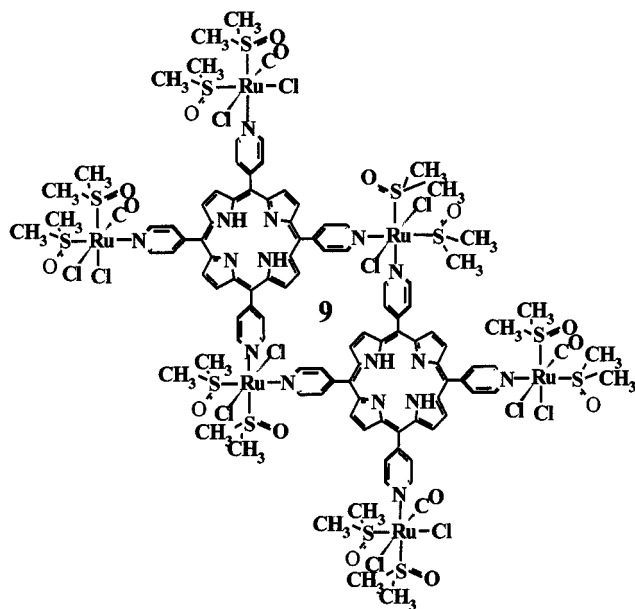


Figure 4. Schematic representation of *trans,cis,cis*-[RuCl₂(DMSO-*S*)₂{*cis*-4'-TPyP([Ru])₂}₂] (9)

trum) were thus attributed to the 4'(N)py–Pd rings; these assignments also agree well with those reported by Stang and co-workers for the corresponding [2+2] molecular square, [Pd(dppp){4'-*cis*DPyP}₂(OTf)₄] (7), prepared by reaction of equimolar amounts of 4'-*cis*DPyP and 4.^[7] It should be noted that formation of [Pd(dppp){*cis*-4'-TPyP([Ru])₂}₂(OTf)₄] (6) involves a slight upfield shift of the H_{3,5} resonance of the previously unbound 4'(N)py rings in 2. Moreover, in 6 one singlet and, in particular, one doublet of the β-H resonances on each porphyrin are remarkably upfield shifted also; these signals are correlated by clear NOE cross-peaks to the H_{3,5} 4'(N)py–Pd signal in the NOESY spectrum. Similar anomalously upfield resonances for the protons closest to Pd were found in the ¹H NMR spectra of 7^[7] and of the heterobimetallic Ru^{II}–Pd^{II} cyclic assemblies [Pd(dppp){*trans,cis,cis*-RuCl₂(X)(Y){4'-*cis*DPyP}₂}₂](OTf)₂ (X, Y = DMSO-*S*, CO)^[9] and were attributed by us to the shielding cone of the phenyl rings of the dppp ligand rather than to the Pd^{II} center.^[9] This hypothesis is confirmed here by the NMR spectrum of the [2+2] square of rimmed porphyrins [Pd(PEt₃)₂{*cis*-4'-TPyP([Ru])₂}₂](OTf)₄ (8), closely related to 6 and prepared by treatment of 2 with one equivalent of *cis*-[Pd(PEt₃)₂](OTf)₂. In 8, which lacks the shielding phenyl rings on the phosphanes, the resonances of the pyrrole protons closest to Pd and those of the 4'(N)py–Pd rings are remarkably more downfield-shifted than in 6 (e.g. δ H_{3,5} = 8.62 in 8 vs. 8.16 in 6).

Finally, the neutral molecular square of porphyrins rimmed with ruthenium coordination compounds *trans,cis,cis*-[RuCl₂(DMSO-*S*)₂{*cis*-4'-TPyP([Ru])₂}₂] (9, Figure 4) was prepared by treatment of 2 with one equivalent of *trans*-[Ru^{II}Cl₂(DMSO-*S*)₄] (5). Metallacycle 9 features two types of Ru^{II} centers with different coordination environments and roles: *trans*Ru moieties are located at the two cor-

ners of the square, while four [Ru] units rim the periphery of the square. Coordination of 2 to the *trans*Ru moiety affected mainly the H_{2,6} and H_{3,5} resonances of the 4'-N(py) ring involved in the new bonds, which experienced downfield shifts similar to those found in the corresponding *trans,cis,cis*-[RuCl₂(DMSO-*S*)₂{4'-MPyP}₂] complexes.^[9–11]

Conclusion

In conclusion, we have demonstrated that new families of cationic and neutral multiporphyrin metallacycles, in which the porphyrins are externally decorated with Ru^{II} complexes, are readily assembled through the formation of coordination bonds between partially ruthenated 4'-TPyP and either square planar Pd^{II} or octahedral Ru^{II} auxiliaries, respectively.

The higher degree of complexity of the new molecular squares of porphyrins rimmed with coordination compounds compared to the previously known multichromophore cyclic assemblies requires a more demanding synthetic approach (mainly in terms of purification of the partially metalated porphyrins) but also offers exciting perspectives: in future a proper choice of the external and of the structural metal centers (corners of the square) might favor electron and/or charge transfer from one site to another within the assembly. Moreover, the external metal centers might be exploited for incorporating special properties (e.g. chirality, luminescence, ...) into the multiporphyrin cyclic assembly and for its further functionalization. For the time being, since the main focus of the present work was directed towards the establishment of a synthetic approach for such novel cyclic assemblies, only metal compounds with a well-known and tested chemistry were used both as structural and rimming units.

Experimental Section

¹H and ³¹P{¹H} NMR spectra were recorded on a Jeol EX400 spectrometer at 400 and 161.9 MHz, respectively. The ¹H NMR signals were referenced to the signal of residual CHCl₃ (δ = 7.26) and assignments were made with the aid of 2D COSY experiments, as detailed in the text; ³¹P NMR spectra were referenced to external H₃PO₄. ES-MS data were obtained on a Perkin–Elmer API spectrometer. Samples were dissolved in chloroform; the spectra were recorded in the positive ion mode at 5.6 kV accelerating potential; 2% trifluoroacetic acid was added to the solutions of 2 and 3. The UV/Vis spectra were obtained on a Jasco V–550 spectrophotometer. All reagents were analytical grade.

Preparation of *cis*-4'-TPyP([Ru])₂ (2) and *trans*-4'-TPyP([Ru])₂ (3): The reaction between 4'-TPyP and *cis,trans*-RuCl₂(DMSO)₃(CO) (1) was performed as reported in ref.^[11] Components of the mixture were separated by column chromatography on silica gel;^[11] the two bis-ruthenated isomeric products, *cis*-4'-TPyP([Ru])₂ (2) and *trans*-4'-TPyP([Ru])₂ (3), were obtained as a mixture from the column and their separation required further preparative-scale TLC on silica gel plates (CH₂Cl₂/EtOH mixture 90:10; *R_f* 2 = 0.81, *R_f* 3 = 0.84). The products were extracted from the silica with an acetone/MeOH mixture (80:20). 100 mg of 4'-TPyP yielded, on average, 11 mg each of isolated 2 and 3 (5%). Elemental analyses for 2 and

3 were not reliable because they were affected by the presence of variable amounts of solvent molecules of crystallization.

Selected data for **2**: ^1H NMR (CDCl_3): $\delta = -2.96$ (s, 2 H, NH), 3.62 (s, 6 H, DMSO-*S*), 3.64 (s, 6 H, DMSO-*S*), 3.69 (s, 12 H, DMSO-*S*), 8.19 [m, 4 H, H3,5(py)], 8.22 (m, 4 H, H3,5[Ru]), 8.86 (s, 2 H, β -H), 8.88 (d, $^3J = 8$ Hz, 2 H, β -H), 8.91 (d, $^3J = 8$ Hz, 2 H, β -H), 8.95 (s, 2 H, β -H), 9.09 [m, 4 H, H2,6(py)], 9.51 (m, 4 H, H2,6[Ru]). – UV/Vis (CH_2Cl_2): λ ($\epsilon \times 10^4/\text{M}^{-1} \text{cm}^{-1}$) = 419 (28), 514 (1.5), 549 (0.6), 589 (0.5), 645 (0.2) nm.

Selected data for **3**: ^1H NMR (CDCl_3): $\delta = -2.97$ (s, 2 H, NH), 3.62 (s, 6 H, DMSO-*S*), 3.64 (s, 6 H, DMSO-*S*), 3.69 (s, 12 H, DMSO-*S*), 8.17 [m, 4 H, H3,5(py)], 8.22 (m, 4 H, H3,5[Ru]), 8.88 (d, $^3J = 4$ Hz, 4 H, β -H), 8.92 (d, $^3J = 4$ Hz, 4 H, β -H), 9.09 [m, 4 H, H2,6(py)], 9.50 (m, 4 H, H2,6[Ru]). – UV/Vis (CH_2Cl_2): λ ($\epsilon \times 10^4/\text{M}^{-1} \text{cm}^{-1}$) = 419 (38.5), 515 (2.2), 549 (0.8), 589 (0.7), 645 (0.3) nm.

Preparation of [Pd(dppp){cis-4'-TPyP([Ru])₂}]₂(OTf)₄ (6**), [Pd(PEt₃)₂{cis-4'-TPyP([Ru])₂}]₂(OTf)₄ (**8**), and trans,cis,cis-[RuCl₂(DMSO-*S*)₂{cis-4'-TPyP([Ru])₂}]₂ (**9**):** Owing to the very low amounts of precursor **2** (few mg), reactions leading to molecular squares **6**, **8**, and **9** were performed exclusively in an NMR tube. The formation of **6** and **8** occurred rapidly, while the formation of **9** required three hours at ambient temperature. The electronic spectra of **8** and **9** are qualitatively very similar to that of **6** (see below) in terms of the shape and position of the absorption bands, but the purity of the products isolated from the NMR solutions upon removal of the solvent (established by NMR spectroscopy) was not deemed high enough for quantitative measurements (determination of absorption coefficients).

Selected data for **6**: ^1H NMR (CDCl_3): $\delta = -3.16$ (s, 4 H, NH), 3.63 (s, 12 H, DMSO-*S*), 3.69 (s, 12 H, DMSO-*S*), 8.16 (m, 8 H, H3,5Pd), 8.21 (m, 8 H, H3,5[Ru]), 8.38 (d, $^3J = 4$ Hz, 4 H, β -H), 8.58 (s, 4 H, β -H), 8.92 (s, 4 H, β -H), 8.94 (d, $^3J = 4$ Hz, 4 H, β -H), 9.52 (m, 8 H, H2,6[Ru]), 9.86 (m, 8 H, H2,6Pd). – ^{31}P NMR (CDCl_3): $\delta = 6.1$. – UV/Vis (CH_2Cl_2): λ ($\epsilon \times 10^4/\text{M}^{-1} \text{cm}^{-1}$) = 424 (52.0), 518 (3), 553 (1), 592 (0.6), 646 (0.1) nm.

Selected data for **8**: ^1H NMR (CDCl_3): $\delta = -2.98$ (s, 4 H, NH), 3.65 (s, 12 H, DMSO-*S*), 3.70 (s, 6 H, DMSO-*S*), 3.71 (s, 6 H, DMSO-*S*), 8.22 (m, 8 H, H3,5[Ru]), 8.56 (d, $^3J = 4$ Hz, 4 H, β -H), 8.62 (m, 8 H, H3,5Pd), 8.87 (s, 4 H, β -H), 8.94 (d, $^3J = 4$ Hz, 4 H, β -H), 9.01 (s, 4 H, β -H), 9.52 (m, 8 H, H2,6[Ru]), 10.18 (m, 8 H, H2,6Pd). – ^{31}P NMR (CDCl_3): $\delta = 21.5$.

Selected data for **9**: ^1H NMR (CDCl_3): $\delta = -2.89$ (s, 4 H, NH), 3.71, 3.70, 3.66, 3.64 (s, 72 H, DMSO-*S*), 8.25 (m, 8 H, H3,5[Ru]), 8.39 (m, 8 H, H3,5Ru), 8.96 (m, 8 H, H- β), 9.00 (m, 4 H, H- β), 9.03 (s, 4 H, H- β), 9.55 (m, 8 H, H2,6[Ru]), 10.10 (m, 8 H, H2,6Ru).

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- [6] Abbreviations: *meso*-4'-pyridylporphyrins (4'-PyPs); 5,10-bis(4'-pyridyl)-15,20-diphenylporphyrin (4'-cisDPyP); 5,15-bis(4'-pyridyl)-10,20-diphenylporphyrin (4'-transDPyP); 5,10,15,20-tetra(4'-pyridyl)porphyrin (4'-TPyP).
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- [12] As it is often the case with pyridylporphyrins, the broadening of the H2,6 and H3,5 resonances in the ^1H NMR spectrum of compound **2** is due to the presence in solution of small amounts of Lewis acids, in this case very likely silica from the chromatographic purification of **2**. The weak and labile interaction between the uncoordinated pyridyl rings of compound **2** and the Lewis acid induces a broadening (and a very small shift) of the proton resonances of such rings.
- [13] Since the [Ru] moiety is chiral, both **2** and **3** must exist as mixtures of stereoisomers (with *C* or *A* [Ru] units), with potentially different NMR signals. However, at the field used, the ^1H NMR signals were not distinct for the diastereoisomers.

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