Random two-dimensional string networks based on divergent coordination assembly

Matthias Marschall^{1,2}, Joachim Reichert^{1,2}, Alexander Weber-Bargioni², Knud Seufert¹, Willi Auwärter¹, Svetlana Klyatskaya³, Giorgio Zoppellaro³, Mario Ruben^{3,4}* and Johannes V. Barth^{1,2}*

The bulk properties of glasses and amorphous materials have been studied widely, but the determination of their structural details at the molecular level is hindered by the lack of long-range order. Recently, two-dimensional, supramolecular random networks were assembled on surfaces, and the identification of elementary structural motifs and defects has provided insights into the intriguing nature of disordered materials. So far, however, such networks have been obtained with homomolecular hydrogen-bonded systems of limited stability. Here we explore robust, disordered coordination networks that incorporate transition-metal centres. Cobalt atoms were co-deposited on metal surfaces with a ditopic linker that is nonlinear, prochiral (deconvoluted in three stereoisomers on two-dimensional confinement) and bears terminal carbonitrile groups. *In situ* scanning tunnelling microscopy revealed the formation of a set of coordination nodes of similar energy that drives a divergent assembly scenario. The expressed string formation and bifurcation motifs result in a random reticulation of the entire surface.

Inderstanding the nature of condensed disordered systems represents one of the challenging tasks for twenty-first century science¹⁻⁴. Traditional experimental tools that rely on ensemble averaging have provided many important insights into the fascinating properties of glasses and amorphous solids, but to identify local order characteristics requires imaging techniques that address the individual constituents and topological defects. The direct, molecular-level investigation of random networks became possible with two-dimensional (2D) supramolecular systems assembled on well-defined surfaces amenable to *in situ* observation using scanning tunnelling microscopy (STM).

For instance, a series of elementary structural motifs that reflect hydrogen-bonding multiplicity was identified in kinetically trapped random networks obtained with nonsymmetrical cytosine molecules on a Au(111) surface under vacuum conditions at low temperatures⁵. At solid–liquid interfaces, rod-like molecular building blocks with four peripheric, isophthalic functional endgroups were shown to form porous networks that displayed orientational symmetry, but simultaneously lacked large-scale translational order^{6,7}. Such molecular random tilings, in which the density of spatially fluctuating defects is rather low, can be regarded as entropically stabilized phases that represent 2D glasses^{6,8}.

Here we report an STM investigation of robust, disordered coordination networks that comprise interconnected polymeric strings and multiple ramification motifs. We used a nonlinear prochiral ditopic linker deconvoluted in three stereoisomers on surface confinement (Fig. 1). Coordination assembly was induced by co-deposited cobalt atoms, which engaged in lateral metal-ligand interactions with the linker dicarbonitrile endgroups. The resulting complex networks are based on a set of distinct three-and fourfold cobalt–carbonitrile nodal coordination motifs of similar energy that result in bifurcation or string formation. Thus, symmetry deconvolution of the linker and coordination multiplicity entails divergent assembly with concomitant random reticulation of

the entire surface. An important feature of coordination interactions is their appreciable bonding strength, typically significantly higher than that of hydrogen bonds. In the present study this is exploited to meet the important criterion of room-temperature stability regarding open, random networks—namely irregular, 2D, reticulated surface architectures that comprise voids.

For our investigations we relied on the principles of surface-confined supramolecular coordination chemistry^{9,10}, a new strategy for the fabrication of low-dimensional molecular architectures¹¹. Notably, this methodology was used to design regular nanoporous networks that contained well-defined and tunable cavities¹²⁻¹⁴. Furthermore, coordination chains or polymers have been reported for several systems, and typically reflect a template assembly with well-defined metal-ligand binding motifs and directional order, both under vacuum and at the solid–liquid interface^{15–23}. In addition, surface-confined hierarchic^{24,25}, autocorrective²⁶ or fractal²⁷ complex nanoarchitectures were obtained. With these systems, once the design principles are rationalized, the regular structural outcome can be anticipated and thus is associated with convergent synthesis²⁸—namely a metal-directed assembly that provides high yields and well-defined supramolecular coordination modules, polymers or networks.

The highly symmetric ditopic or tritopic linkers used thus far on low-index metal surfaces favour the encountered convergent protocols, in which a unique or a small number of bonding motifs within the formed structures are at the origin of extended, regular supramolecular arrangements. Thus, translational symmetry, size and shape control can be achieved for polymeric or network structures. By contrast, with the nonlinear prochiral linker used at present the symmetry-breaking effect of the surface, in conjunction with the predominant, coexisting three- and fourfold coordination nodes that are close in energy, generates a multiplicity of distinct network elements that do not organize in a regular pattern. Because the ditopic linker's functional endgroups are at its periphery, many

¹Physik Department E20, TU München, James-Franck Strasse, D-85748 Garching, Germany, ²Department of Physics & Astronomy, University of British Columbia, Vancouver, 2355 East Mall, V6T 1Z4, Vancouver, Canada, ³Institut für Nanotechnologie, Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany, ⁴IPCMS-CNRS UMR 7504, Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France. *e-mail: mario.ruben@kit.edu; johannes.barth@ph.tum.de



Figure 1 | **Deconvolution of the prochiral molecular linker [1,1';4',1'']-terphenyl-3,3''-dicarbonitrile on 2D confinement. a-c**, The rotatability around the phenyl backbone axis, indicated by the black arrows, accounts for the three different surface conformers, the *cis*- (**a**), *L*-*trans* (**b**) and mirror-symmetric *D*-*trans* (**c**) arrangements. Light blue spheres: C; dark blue spheres: N; white spheres: H.



Figure 2 | **STM images of random coordination string networks. a,b**, The co-deposition of cobalt atoms and nonlinear dicarbonitrile linkers on close-packed Ag(111) (a) and Cu(111) (b) surfaces leads to the formation of random networks. Sample bias voltage (V_B) = 1.2 V, tunnelling current (I_T) = 0.1 nA; recorded at 300 K. Scale bars: 10 nm.

different interconnection modes between network elements are expressed, which represent either coordination strings or bifurcation nodes. We thus designate the pertaining coordination-assembly model as divergent; that is, associated with irregular morphological features and intrinsic random characteristics.

Random network formation

Specifically, we used a ditopic linker, the rod-like *p*-terphenyl-*m*dicarbonitrile **1** (*m*NC-Ph₃-*m*CN) (Fig. 1), with a distance of 12.56 Å between the terminal nitrogen atoms of the carbonitrile moieties. This nonlinear species comprises three phenyl rings that are rotatable around the respective interconnecting carbon–carbon σ -bonds. At each outer phenyl ring a carbonitrile group is attached in the *meta* position to form a 60° angle with respect to the terphenyl backbone orientation. On adsorption, the prochiral molecule deconvoluted into a *cis–trans* diastereomeric mixture, which included two differentiable D- and L-*trans* enantiomers, by the symmetry-breaking effect of the surface. On the level of stereoconformers the natural composition of the pertaining 2D fluid at low coverages can be assumed to be 50% *cis* and 25% for each of the mirror-symmetric *trans* conformations.

STM overview images of typical coordination networks after cobalt-directed assembly of the linkers on Cu(111) and Ag(111) are reproduced in Fig. 2. The data reveal irregular networks on both surfaces, which consist of meandering strings interconnected by a variety of nodes. The networks do not display mesoscale order, in marked contrast to the highly regular nanomeshes obtained with ditopic linear linker analogues^{13,14}. However, they are built up by a limited number of distinct coordination motifs and present coordination

nodes that clearly show short-range order. Accordingly, they can be designated as 2D, glassy coordination networks.

The formation of very similar random networks on substrates with $\sim 10\%$ difference in surface lattice constants (4.08 versus 3.55 Å) indicates construction principles whereby the epitaxial fit does not have a decisive role in the structural evolution. Therefore, the assembly of pure linker layers on both substrates gives densely packed extended islands, the order of which reflects non-covalent lateral interactions between carbonitrile endgroups and aromatic moieties²⁹. The island formation and their stepedge fluctuation at 300 K (see Supplementary Fig. S1) give further evidence that high molecular mobility prevails during the coordination assembly conducted in the 300-350 K range. The morphology of the random networks presented here is thus dominated by the availability of different conformers and adaptive coordination motifs. The compact protrusions in Fig. 2 are small cobalt clusters that show cobalt excess during network formation; that is, metalcentre deficiency can be ruled out as a factor that determines network characteristics.

Coordination motifs and network morphology

A high-resolution STM image that reveals molecular positioning within the coordination strings and their intersections is reproduced in Fig. 3. First, here we can identify and assess the distribution of surface conformers. A statistical analysis of random coordination networks performed for a series of such images revealed that the natural ratio of a 2D surface gas is roughly conserved ($\sim 60\%$ *cis* and $\sim 20\%$ for each *trans* species). The slight deviation detected from the ideal composition might be caused, in part, by

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Figure 3 | Molecular-resolution STM images of a disordered coordination network on Ag(111). a, Coordination motifs that underlie the random network with coexisting three- and fourfold coordination nodes. $V_B = 1.2 \text{ V}$, $I_T = 0.1 \text{ nA}$; recorded at 8 K. Scale bar: 5 nm. **b-e**, Magnified views (**b**,**d**) showing the dominant bifurcation motifs (circled) with their corresponding models, *cis-cis-Co-trans-trans* bifurcation (**c**•*tt*) (**c**) and Co-*trans-trans* bifurcation (•*ttt*) (**e**). Scale bar: 1 nm. Light blue spheres: C; dark blue spheres: N; white spheres: H; orange spheres: Co.

diastereomeric discrimination during gas-phase deposition related to the mutual orientation of functional groups and the small cistrans conversion barrier (6 kJ mol⁻¹) related to a carbon-carbon biphenyl rotation³⁰. This indicates that during network assembly the linkers rarely change their conformation and are stabilized preferentially by surface and lateral interactions. Second, the data clearly reveal the coexistence of nodal motifs with three- or fourfold coordination of cobalt centres by carbonitrile ligands. The encountered coordination nodes can be separated into bifurcation motifs and chain motifs, which occur for three- and fourfold cobalt coordination. The predominant bifurcation motifs are of the fourfold cis-cis-Co-trans-trans (labelled $cc \bullet tt$) and the threefold Co-trans-trans (•ttt) node families (Fig. 3b,d). Their corresponding models are given in Fig. 3c,e, respectively, and were found in our data sets in both possible mirror-symmetric configurations (see Supplementary Information).

Furthermore, formation of the random string network requires the existence of chain motifs. They are identified readily in Fig. 4, but are even more pronounced in preparations at slightly reduced coverages, such as that depicted in Fig. 4a. The predominant chain-forming coordination nodes are of the families *cis-cis*-Co*cis-cis* ($cc \bullet cc$, modelled in Fig. 4e) and *cis-cis*-Co-*trans* ($cc \bullet t$, modelled in Fig. 4f).

The proportion of threefold-coordinated nodes in a given network is typically significantly higher than that of fourfold-coordinated nodes, which is supported by density functional theory results that indicate an energetic preference for threefold coordination of cobalt centres by carbonitrile functional groups on noble metal surfaces. The calculations revealed that in the presence of a silver substrate (modelled by a silver cluster) this preference is the result of a small energy difference between three- and fourfold cobalt coordination of only 90 meV per coordination node (in contrast to the situation for isolated planar nodes, in which the preference is inverted in favour of fourfold coordination)¹³. The pertaining binding energies per ligand amount to ~0.7 and ~0.5 eV for threefold versus fourfold coordination, respectively; taking into account the bonding to the subjacent silver cluster, a small total energy difference results.

Importantly, the calculations apply equally well to linear and bent linkers because the change in symmetry does not affect the arrangement of the functional groups in direct proximity to the coordination node. For steric reasons, molecular strings that incorporate a sequence of three- or fourfold coordination nodes cannot be realized with the linear linkers. In the case of linear dicarbonitrile molecules, the energy difference thus promotes highly regular honeycomb structures that exclusively feature threefold coordination after the convergent coordination assembly at room temperature^{13,14}. Only under conditions associated with kinetic limitations (~250 K, see Supplementary Fig. S2) was the expression of a defective honeycomb structure with a minority of fourfold coordination nodes observed (that is, self-correction with the elimination of defective arrangements is fully operational at 300 K). By contrast, the formation of random networks with bent linkers under conditions in which yet higher energy barriers can be overcome (temperatures up to 350 K), in conjunction with their high surface mobility and the similarity of the coordination motifs, signals that kinetic limitations do not dominate the ordering scenario. Thus, the small energy difference, in combination with the stereochemical deconvolution of the different molecule configurations (an opportunity not present for the linear equivalents), favours the expression of random string networks.

The predominance of a set of specific coordination motifs and the expression of a random, reticulated structure that spreads out over large areas reflects a dynamic, divergent assembly scenario, in which the reversibility of the metal–ligand interactions interferes decisively. This directly contrasts the principles that underlie the onsurface synthesis of branched polymeric nanostructures, which are trapped kinetically and have geometric properties dictated by the irreversible formation of covalent bonds^{31–33}. Accordingly, there are to date no reports of covalent bond formation on surfaces used to fabricate well-ordered molecular nanoarchitectures.

Statistics and 2D chirality considerations

A coordination-node statistical analysis derived from data series representative of the situation depicted in Fig. 3 is shown in Table 1. For simplicity, the *cis*- and *trans*-enantiomers (rather than the *cis*-, D-*trans*- and L-*trans*-enantiomers) are pooled. The dominating chain motifs ($cc \circ c$, $cc \circ t$ and $cc \circ cc$) represent ~50% of the realized possibilities, and predominant bifurcation motifs ($cc \circ tt$, $\circ ttt$, $\circ ttt$, $cc \circ ct$ and $\circ tttt$) account for ~43%. Linkers attached to cobalt clusters were excluded, and ~5% of the nodes have coordination numbers that exceed four.

A surprising result of the network-node analysis is that motifs equivalent from purely statistical considerations do not appear



Figure 4 | **Random coordination string networks on Ag(111). a**, High-resolution STM image that emphasizes the string characteristics on Ag(111). $V_B = 1.2 \text{ V}$; $I_T = 0.1 \text{ nA}$; recorded at 8 K. Scale bar: 5 nm. **b**,**c**, Magnified chain with a threefold cobalt-coordination motif (**b**, circled) and a schematic representation of the corresponding *cis-cis*-Co-*cis* (*cc*•*c*) kink (**c**). Scale bar: 1 nm. **d-f**, Magnified chain with fourfold cobalt-coordination motifs (**d**, circled) and schematic representations of the circled kinks, *cis-cis-Co-cis* (*cc*•*c*) chain motif (**e**) and two mirror-symmetric configurations of *cis-cis*-Co-*trans* (*cc*•*t*) bifurcation motifs (**f**). Scale bar: 1 nm. Light blue spheres: C; dark blue spheres: N; white spheres: H; orange spheres: Co.

with equal probability. For instance, the units required to build either *cct* or *ctt* configurations are similarly abundant in a 2D fluid of linkers. The evident preference for the chaining $cc \bullet t$ unit after coordination with cobalt must be associated with the selection mechanisms that operate during the network assembly, which presumably implies, for instance, the interference of mobile metalmolecule subunits³⁴, and rotational movements of the (coordinated) linkers or weak lateral interactions between them, for example between carbonitrile groups and aromatic moieties²⁹. For a full clarification of this intriguing behaviour further studies of network formation *in situ* and of complementary kinetic Monte-Carlo simulations are suggested.

Furthermore, 2D chirality represents an additional central aspect for the network topology, because the expression of the coordination nodes accounts for organizational chirality^{35,36}, which has topological consequences. For instance, either left- or right-handed windmill motifs can be realized with mononuclear, threefold cobalt coordination by *cis*-conformers on surfaces (model given in the Supplementary Information). Consequently, the families summarized in Table 1 present a library of 90 different coordination motifs in total, following the concept presented by Lehn³⁷. The complete tabulation of all nodes with differentiated chirality signatures provided in the Supplementary Information shows that the families of three- and fourfold coordination nodes provide 20 and 70 motifs, respectively.

This dynamic library is available, in principle, for network formation and allows many surface reticulation possibilities. Thus, the interplay of local order induced by the metal–ligand interactions and the multiple levels of isomerism and chirality creates a topological conundrum to which the system's response is random reticulation. Accordingly, in contrast to the scenario of highly convergent, metal-directed surface coordination assembly with linear dicarbonitrile species^{13,14}, the 2D stereoisomerism of the linker discussed

Table 1 | Coordination-node statistics that summarize the possible families of three- and fourfold nodal motifs.

Families of threefold coordination nodal motifs

cc•c	9 %
cc•t	36%
• ctt	<1%
•ttt	7%
Proportion of the total number of coordination motifs	\sim 53%
Families of fourfold coordination nodal motifs	
cc∙cc	5%
cc∙ct	5%
cc•tt	27%
ct•tt	<1%
•tttt	4%

2D chirality of pertaining conformers and nodal motifs are pooled, the dominating chain motifs are given in bold and the amount of higher coordinated nodes is minor and has been neglected.



Figure 5 | **Molecular manipulation experiments. a**,**b**, A linker at the end of a coordination string was manipulated with a STM tip (performed at 8 K) to flip it between the initial (**a**) and final states (**b**) as the tip was moved laterally across the terminal molecule. **c**,**d**, The displacement of the entire chain segment is shown. Imaging parameters, $V_B = -0.2$ V, $I_T = 0.11$ nA; for manipulation, $V_B = -50$ mV, $I_T = 20$ nA. Scale bars: 2 nm.

instructs a divergent assembly route. The use of a 2D chiral linker *per se* is not necessarily sufficient for a random network formation; in previous studies we identified cases in which asymmetric molecular backbones merely led to distortions in surface coordination networks that showed a unique nodal motif^{38,39}. Furthermore, chiral coordination nodes, for instance identified in networks with mononuclear iron–phenolate coordination motifs, can account for various cavity types in porous networks⁴⁰.

The node composition found in the amorphous network has to satisfy the natural ratio of available conformers and co-determines the order of the network through the ratio between bifurcation motifs and chain-forming motifs. Whereas highly ordered structures that contain the natural ratio between the three surface conformers can be proposed (see the phase shown, as an example, in the Supplementary Information), the inherent disorder of networks reported here is evidence for a 2D glassy state-that is, its constituents congeal during network formation and do not achieve a regular phase. Consequently, free-energy minimization during network formation does not bestow a homogeneous super lattice, in striking contrast to the high regularity achieved with linear building blocks and identical local coordination interactions. Taking into account the potientating effect on the number of nodal motifs that arise from symmetry considerations (see tabulation in the Supplementary Information), the weight of the entropic term must be affected substantially by the chiral nature of the linkers. It is suggested that this term (beyond the binding-energy consideration of elementary structural motifs⁵ (see the discussion above)) is of general importance in the expression of 2D supramolecular random networks^{6,8}.

For the string networks discussed here, a further characteristic of the coordination motifs is metal–ligand bond length. The linker's electronic structure is affected only weakly by the subjacent silver lattice^{13,14,41}, so we can assume that the encountered conformers are close to the geometry of isolated species. The models represented in Figs 3 and 4 take this into account, on the basis of which we estimate a cobalt–carbonitrile bond distance of ~2 Å, similar to values found for 2D cobalt–carbonitrile nanomeshes with linear linkers^{13,14} and related 3D compounds⁴². In isolated coordination compounds or 3D networks, changes in electronic properties are expected with different coordination numbers. In agreement, the STM measurements also point to differences regarding the electronic structure of threefold versus fourfold coordinated metal centres. Whereas typically the latter are imaged as protrusions (that is, provide a substantial contribution to the surface local density of states), the cobalt atom with triple carbonitrile coordination is mostly transparent^{13,14}. This signals the existence of a 2D analogue to conventional bulk, mixed-valence coordination polymers or networks, although one must keep in mind that the electronic structure of the cobalt centres is influenced by the underlying metal substrate^{9,10,43}.

Molecular manipulation with an STM tip

To obtain further insight into the nature of the coordination strings and nodes, molecular manipulation experiments were carried out. To this end, in constant-current mode the STM tip was moved laterally across a molecule that terminated a chain segment. Thereby, the tip-sample distance controlled by the tunnelling resistance Rwas reduced, starting from normal imaging conditions in which the network is generally unaffected by the scanning procedure $(R = 1.8 \text{ G}\Omega)$ and continuing until a displacement of the molecule was observed ($R = 2.5 \text{ M}\Omega$). In Fig. 5 we compare selected states prior to and after such manipulation steps. Figure 5a,b indicate that the terminal molecule can flip during the manipulation procedure while being attached to the linking node continuously, as the observed change in angle is consistent with a rotation of the linker about the carbonitrile-cobalt connection. Figure 5c,d demonstrate the displacement of an entire string, which is leveraged about a threefold coordination mode without breaking. Thus, the lateral metal-ligand interactions override the substrate bonding at specific sites, which confirms the minor impact of the surface atomic lattice on the random networks. It is suggested that this important feature gives the flexibility apparently required for network assembly. To introduce structural flexibility in surface-confined supramolecular arrangements an alternative possibility is the use of flexible molecular species, with which a certain level of adaptiveness can also be achieved⁴⁴⁻⁴⁶.

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It is interesting to compare our findings with the recently reported hydrogen-bonded random networks from cytosine molecules assembled on the Au(111) surface⁵. With this system, multiple elementary coupling motifs, notably different hydrogenbonded filament and ring arrangements of the flat-lying molecules, could be identified also. The mutual orientation of the network constituents is determined by the availability of many hydrogen-bond donor and acceptor groups within the same molecule. By contrast, the coordination nodal motifs presented here are based on the interaction of just one functional molecular endgroup and single metal adatoms. Thus, they give different local, short-range order characteristics (that is, the regular arrangement of carbonitrile groups around cobalt centres), and both the disposition for ramification and string formation can be explained by the linker asymmetry and organizational chirality. Furthermore, the embedded metal centres represent coordinatively unsaturated sites9,10 that can provide distinct functional properties⁴³. In addition, the higher stability of cobalt-nitrogen coordinative bonds compared to the weak hydrogen bonds used previously⁵ means that room-temperature stability of the open, disordered topology formed is achieved. This is an important aspect in view of the potential applications of 2D glassy coordination networks.

Conclusion

We report here a full spatial and structural elucidation of disordered coordination architectures using STM to probe directly the arrangements at the molecular level. Our results reveal the divergent assembly of random string networks on planar surfaces using a prochiral, ditopic linker that forms metal-ligand bonds with cobalt centres. The use of coordination interactions renders robust disordered network structures that incorporate distinct bifurcation and string motifs based on a scenario mediated by reversible metal-ligand interactions. The connection between molecular symmetry, onsurface metal-ligand interactions and energetic similarity of the predominant three- and fourfold coordination nodes provides design criteria for the engineering of disordered 2D solids. It is suggested that string networks with randomization and multiple coordination motifs present a new route towards a distinct class of robust, adaptive compounds and network topologies situated between so-called metal-organic frameworks and covalent polymers.

Methods and materials

The synthesis of the rod-like *m*NC-Ph₃-*m*CN (1) molecule was developed according the published procedure by coupling *bis*-iodobenzene and two equivalents of 3-phenylboronic acid under typical Suzuki conditions with 10 mol% Pd(0) (ref. 47). The geometry of the free molecule was calculated in the semi-empirical AM1 framework.

The experiments were performed using two custom-designed ultrahigh-vacuum systems (base pressure 1×10^{-10} mbar) that hosted a variable-temperature (Aarhus type⁵ and see www.specs.com) and a low-temperature STM (see www.lt-stm.com), respectively. The used Cu(111) and Ag(111) substrates were prepared by standard procedures (cycles of Ar⁺ sputtering and annealing) to obtain extended, flat terraces separated by monatomic steps. The linkers were deposited from a quartz crucible in an organic molecular-beam epitaxy source at 480 K, with the substrate kept at 300 K. Subsequently, submonolayer molecular films were exposed to a beam of cobalt atoms for the coordination assembly, whereby the linker-metal ratio was adjusted to <3. To equilibrate the resulting surface networks, the samples were annealed to 300–350 K; the higher temperatures led to thermal desorption of linkers not engaged in lateral coordination bonds. After preparation, the sample was transferred *in situ* and STM data were acquired at T=300 K and 6–8 K.

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Author contributions

M.M., J.R., A.W.-B., K.S. and W.A. performed the experiments, and analysed and interpreted the data. S.K. and G.Z. developed the synthesis of the linkers used. J.V.B. and M.R. conceived the studies and co-wrote the paper with W.A., M.M. and J.R.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/ naturechemistry. Reprints and permission information is available online at http://npg.nature. com/reprintsandpermissions/. Correspondence and requests for materials should be addressed to M.R. and J.V.B.