

On Demand: The Singular *rht* Net, an Ideal Blueprint for the Construction of a Metal–Organic Framework (MOF) Platform**

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The need for tunable functional solid-state materials is ever increasing because of the growing demand to address persisting challenges in global energy issues, environmental sustainability, and others.^[1] It is practical and preferable for such materials to be pre-designed and constructed to contain the desired properties and specific functionalities for a given targeted application. An emerging unique class of solid-state materials, namely metal–organic frameworks (MOFs), has the desired attributes and offers great promise to unveil superior materials for many lasting challenges^[2] since desired functionality can be introduced pre- and/or post-synthesis.^[3] A remarkable feature of MOFs is the ability to build periodic structures with in-built functional properties using the molecular building block (MBB) approach, which utilizes pre-selected organic and inorganic MBBs, with desired function, that are judiciously chosen to possess the proper geometry, shape, and directionality required to target given underlying nets.^[4]

An ideal blueprint starts with a net^[5] that: 1) is singular, exclusive for the assembly of given building units; 2) preferably, encloses polyhedral cavities with 3D interconnecting channels; and 3) is not susceptible to self-interpenetration upon net expansion and/or decoration (it should be noted that this confluence into one material is quite rare). Edge-transitive nets (i.e., one kind of edge) are recognized as suitable targets in crystal chemistry,^[6] and, thus, are a prime source to ascertain singular nets for the rational construction

of MOFs. Our analysis of edge-transitive nets revealed an exceptional net, *rht*,^[5] which met all of our requisite criteria.

The *rht* net is singular for the assembly of 24-connected vertices (rhombicuboctahedral (*rco*) vertex figure) and 3-connected vertices (triangular vertex figure). Though triangular MBBs are common in MOF chemistry, we must employ the supermolecular building block (SBB) approach, utilizing externally functionalized metal–organic polyhedra (MOPs) as SBBs, to access the high connectivity *rco* necessary for constructing *rht*-MOFs,^[7] like our original *rht*-MOF-1 (Figure 1). The ability to target a single MOF from

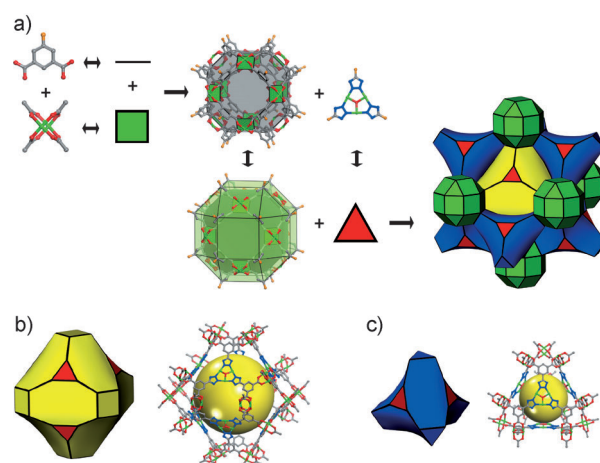


Figure 1. a) Design strategy for the construction of *rht*-MOF-1: Relationship between the MBBs, SBB, and their corresponding building units. b)–c) The two other polyhedral cavities in *rht*-type structures resulting from the cubic packing of the *tcz*-MOP-based rhombicuboctahedral SBB (green).

particular MBBs and SBBs favors platform design and facile tuning. The *rht*-MOF platform can readily be tuned via four basic pathways: 1) expansion of the SBB; 2) spacing of the distance between SBB and triangular MBB; 3) substitution of the triangular MBB; and 4) functionalization.

The first route depends upon expansion of the SBB, which is based on the well-documented^[8] truncated cuboctahedral (*tcz*, $4 \times 12.6 \times 8.8 \times 6$)^[5] MOP. The *tcz*-MOP consists of 12 $\text{Cu}_2(\text{O}_2\text{CR})_4$ (Cu paddlewheels) MBBs joined by 24 isophthalate (1,3-BDC) linkers $[\text{Cu}_{24}(5\text{-R-BDC})_{24}]$,^[9] where the 5-position of each bridging ligand (bent, 120° angle) lies exactly on the vertices of the requisite *rco* (24-connected). Interestingly, to the best of our knowledge, the expanded version of the MOP,

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which can be achieved by positioning isophthalate carboxylates more distal while maintaining the necessary 120° angle, has never been reported, discrete or in **rht**-MOFs. The interior of existing **tcz**-MOPs/SBBs remain relatively inaccessible, and expansion will give unprecedented large pores/cavities.

From the exceptional nature of the **rht**-MOF, based on the singular edge-transitive **rht** net, and ease of synthesis due to controlled formation of the SBB and MBB in situ, it is evident that this platform is amenable, par excellence, to expansion without concern for interpenetration (Figure 2a), as well as building block substitution/decoration and functionalization (i.e., isorecticular chemistry).^[10,11] Herein we report the construction and properties of two novel expanded-SBB **rht**-MOFs, as well as a series of predicted isorecticular **rht**-MOFs with extra-large cavities, and confirm the power of the SBB approach for the deliberate construction of **rht**-MOF as an exemplary platform.

To generate the first **rht**-MOF having expanded SBBs (i.e., expanded **tcz** cavities), we designed and synthesized only the second such tetrazole-based ligand, 5'-(1*H*-tetrazol-5-yl)-1,1':3',1''-terphenyl-4,4''-dicarboxylic acid (**H₃L2**).^[7] Longer benzoate moieties in **L2** replace the carboxylates of **L1**, in **rht**-MOF-1, resulting in increased distance between carboxylates while maintaining the 120° angle, (i.e., expanded isophthalate). As anticipated, reaction between **H₃L2** and Cu^{II} results in the first **rht**-MOF, based on expanded 24-connected SBBs (generated in situ), $[\text{Cu}_6\text{O}(\text{L2})_3(\text{NO}_3)_3 \cdot x\text{solv}]_n$ or **rht**-MOF-2 (Figure 2c). To the best of our knowledge, the discrete **tcz**-MOP based on benzene-1,3-dibenzoate-type linkers has yet to be isolated.^[8]

The unprecedented expanded **tcz**-type SBBs (24 functionalized expanded isophthalate-like ligands connected by 12 Cu paddlewheels), are assembled in situ from the benzene-1,3-dibenzoate moieties. The enclosed cavity has a diameter of 25.7 Å, almost double the size of the original **tcz** built from isophthalate moieties (ca. 15.9 Å; Figure 2b). These extra-large **tcz** are inter-connected through the expected trigonal Cu-oxo trimers formed by each set of three tetrazolate (N_4CR) moieties to give the predicted expanded (3,24)-connected **rht**-MOF.

To further confirm the power of the SBB approach and the uniqueness of the **rht** based MOFs and implement our strategy (i.e., construct an **rht**-MOF with increased distance between the SBB and triangular MBB), we designed and synthesized another novel tetrazolate ligand, 4'-(1*H*-tetrazol-5yl)biphenyl-3,5-dicarboxylic acid (**H₃L3**), where an extra benzene moiety was deliberately placed between the tetrazole and isophthalic termini to increase the distance between the tetrazolate-based MBBs and isophthalate-based SBBs, generated in situ. As anticipated, reaction between **H₃L3** and Cu^{II} produces the expected analogous/isorecticular **rht**-MOF-3, $[\text{Cu}_6\text{O}(\text{L3})_3(\text{NO}_3)_3 \cdot x\text{solv}]_n$ (Figure 2d). As expected, the resulting truncated cuboctahedron cavity remains the same as in **rht**-MOF-1 while the **rdo-a** cavity is enlarged to a diameter of 27.2 Å.

It was evident to us that the trigonal Cu-oxo trimer can be replaced with an organic core while maintaining the isophthalate termini and the essential trigonal positioning

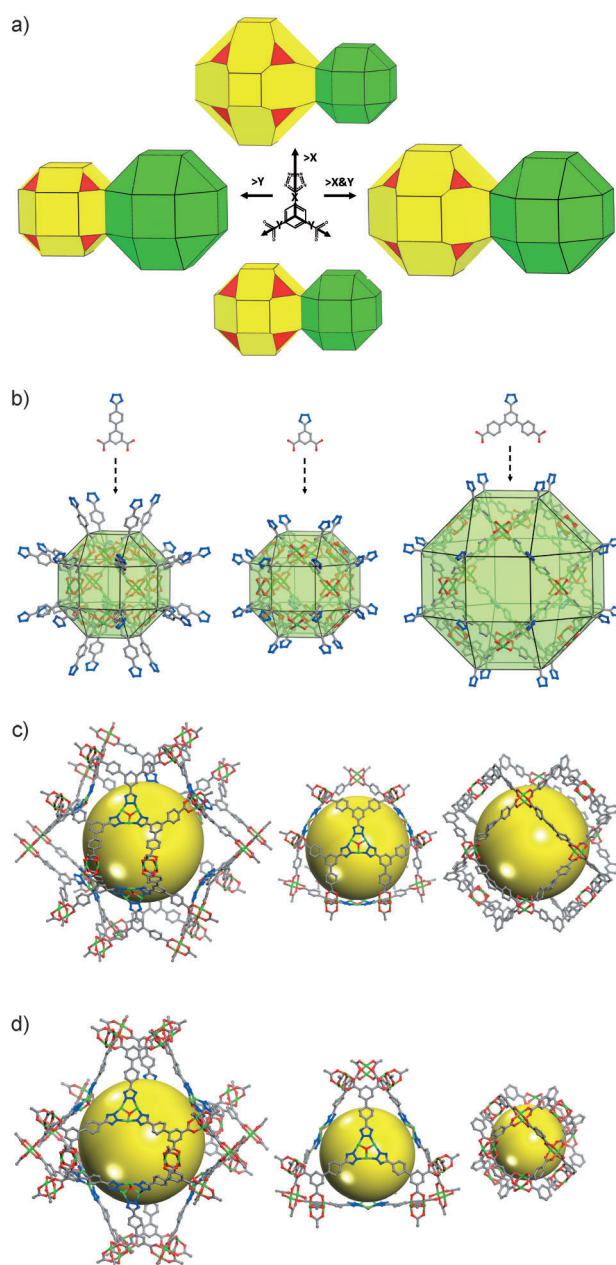


Figure 2. a) The expected increase in size of **rht** structures and related cavities: (bottom) parent **rht**-MOF-1, (left) **rht**-MOF due to expansion along the Y direction; (top); **rht**-MOF due to expansion along the X direction; (right) **rht**-MOF due to expansion along both directions, X and Y. b) (center) **rht**-MOF-1, used as a blueprint for design of new **rht** nets where the length of **H₃L1** has been increased by additional benzene rings in the X direction (left) leading to **rht**-MOF-3 (from **H₃L3**), and in the Y direction (right) leading to **rht**-MOF-2 (from **H₃L2**). Resulting cavities from the representative c) **rht**-MOF-2 and d) **rht**-MOF-3: **rdo-a** (left), **tcu** (center), and expanded **tcz** (right).

thereof, resulting in a trefoil ligand (tL; i.e., trigonal tri-isophthalate ligand; Figure 3a).^[11,12] This feature, raising from the singularity of the **rht** net, is the basis of our third strategy and can be exploited via two different pathways: 1) utilization of trefoil ligands that can permit the construction of **rht**-MOFs based on covalently linked expanded SBBs, which

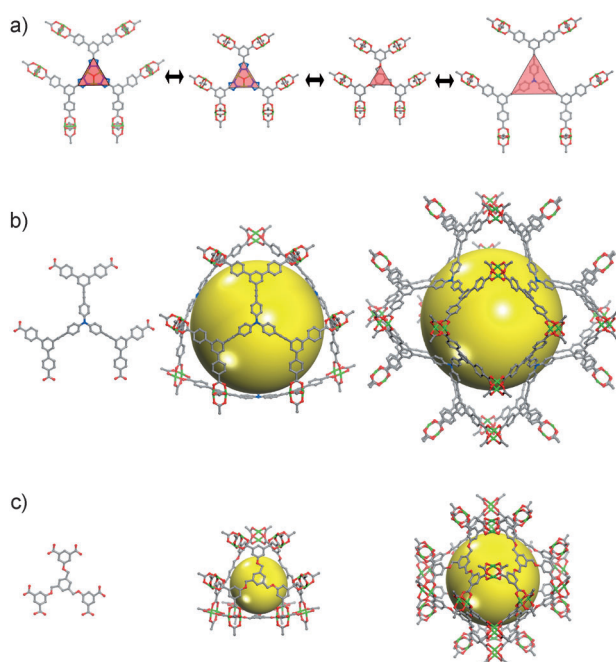


Figure 3. a) Trefoil moieties: The Cu-oxo trimer of the tetrazole-based **rht**-MOFs can be substituted by an organic core. b) Dually expanded trefoil organic ligand, tL3 (left), and select cavities in corresponding **rht**-MOF-6. c) Trefoil tri-isophthalate organic ligand, tL1 (left), and select cavities in corresponding **rht**-MOF-4.

substantiates strategy one; and 2) introduction of flexible trefoil ligands which can impart flexibility into the resulting **rht**-MOF. To apply this third strategy, based on the organic substitution of the triangular inorganic MBB (i.e., tL vs. $\text{Cu}_3\text{O}(\text{L})_3$), several trefoil ligands have been synthesized and utilized to generate **rht**-MOFs.^[7b,11,12]

Herein, we report for the first time the covalent linking of expanded SBBs by introducing a trigonal organic core and replacing the carboxylic acid moieties of an isophthalate terminus with benzoic acid moieties (Figure 3a). To implement this strategy, we designed and synthesized the expanded tris-(4-(5'-ethynyl-1,1':3',1''-terphenyl-4,4''-dicarboxylic acid)-phenyl)-amine ($\text{H}_6\text{tL3}$), which reacts with Cu^{II} to give the expected expanded SBB based **rht**-MOF-6, $[\text{Cu}_3\text{tL3}(\text{H}_2\text{O})_3 \cdot x\text{solv}]_n$ (Figure 3b). The crystal structure is analogous to the previous **rht**-MOFs; however, in this structure the SBBs are covalently (vs. coordinately) interconnected through trigonal tri-substituted organic moieties. Essentially, each central amine core is triply covalently linked through ethynylphenyl moieties to the 5-position of an expanded isophthalate terminus. Thus, all components of the **tcz** cavity in **rht**-MOF-6 remain the same as in **rht**-MOF-2, while the triangular faces of the **rdo-a** and **tcu** cavities are now delimited by purely organic moieties (e.g., $\text{Cu}_{24}[\text{Cu}_3\text{O}(\text{L2})_3]_4(\text{O}_2\text{CR})_{24}$ vs. $\text{Cu}_{24}(\text{tL2})_4(\text{O}_2\text{CR})_{24}$ for the **tcu** cavity; Figure 3a). As expected, all cavities are highly enlarged when compared to **rht**-MOF-1 (25.7 and 16.0 Å vs. 19.1 and 11.8 Å, respectively).

Introduction of the organic triangular core and ability to target specifically **rht**-MOF from our SBB approach allows

the design and synthesis of a flexible **rht**-MOF. To validate this strategy, we utilized the flexible trefoil ligand, 5,5',5''-[1,3,5-phenyl-tris(methoxy)]tris-isophthalic acid {5,5',5''-[1,3,5-benzenetriyltris(methyleneoxy)]tris-1,3-benzenedicarboxylic acid} ($\text{H}_6\text{tL1}$), which reacts with Cu^{II} to give the expected **rht**-MOF-4a or $[\text{Cu}_3\text{tL1}(\text{H}_2\text{O})_3 \cdot x\text{solv}]_n$ (Figure 3c). Due to the comparable trefoil size (Figure 3a), all the cavities in **rht**-MOF-4 are similar in size to the parent **rht**-MOF-1 (15.9, 19.1, and 11.8 Å vs. 15.9, 20.2, and 12.1 Å, respectively).

It should be noted that utilizing trefoil ligands permits the deliberate construction of **rht**-MOFs based only on one type of inorganic MBB, namely the paddlewheel, which eliminates the need to form the Cu-oxo trimer inorganic MBB.^[8] Thus, this route offers potential to assemble **rht**-MOFs with various other metals appropriate for paddlewheel formation,^[8] but not expected to generate a Cu-oxo-like trimer (e.g., Zn and Co). Indeed, reactions between Zn or Co and $\text{H}_6\text{tL1}$ result in isostructural compounds $[\text{Zn}_3\text{tL1}(\text{H}_2\text{O})(\text{DMF})_2 \cdot x\text{solv}]_n$ (**rht**-MOF-4b) and $[\text{Co}_3\text{tL1}(\text{H}_2\text{O})_{1.5}(\text{DMF})_{1.5} \cdot x\text{solv}]_n$ (**rht**-MOF-4c), as determined by comparison of PXRD spectra and/or single-crystal data (Supporting Information, Figure S22). The exceptional versatility of our SBB-based approach and the uniqueness of our **rht**-MOF platform, combined with the vast library of organic syntheses, allow for facile incorporation of multiple desired/targeted functions into the same structure/material.

To prove this concept, we designed and synthesized the azo-functionalized trefoil ligand, 5,5',5''-[4,4',4''-[1,3,5-phenyl-tris(methoxy)]tris-phenylazo]tris-isophthalic acid ($\text{H}_6\text{tL2}$) where a phenylazo link was deliberately placed between the benzene moiety and the isophthalate terminus of tL1. $\text{H}_6\text{tL2}$ reacts with Zn to give the expected dinitrogen-functionalized **rht**-MOF-5, $[\text{Zn}_3\text{tL2}(\text{H}_2\text{O})_3 \cdot x\text{solv}]_n$ (Supporting Information, Figure S17). As anticipated, the extra-large **rdo-a** and **tcu** cavities (25.7 and 16.0 Å vs. 19.1 and 11.8 Å, respectively) are lined with azo moieties. To demonstrate this approach in the tetrazole-based **rht**-MOFs, we designed and synthesized an amide-functionalized tetrazole-based ligand, 5'-(4-(1H-tetrazol-5-yl)benzamido)benzene-1,3-dioic acid ($\text{H}_3\text{tL4}$), which gives the expected **rht**-MOF-8, $[\text{Cu}_6\text{O}(\text{L4})_3(\text{NO}_3) \cdot x\text{solv}]_n$.

The effective implementation of our rational strategy using **rht**-MOF as a platform, where cavity size, shape, and functionality can be controlled and tuned with ease, is evident by the successful design and construction of a series of **rht**-MOFs with some of the lowest framework densities and free volumes reported to date.^[13] Unlike most previous low-density MOFs,^[13] **rht**-MOFs preclude the potential for interpenetration, resulting in one-step, deliberately open frameworks with pores in the mesopore domain.^[14] In fact, calculated free volumes range from about 75% for **rht**-MOF-4 to about 89% for the most open framework of the series, **rht**-MOF-6. The various cavity sizes, apertures dimensions, and accessible free volumes are summarized in the Supporting Information, Table S1, as are surface areas.

The sorption isotherms (i.e., Ar, H_2) for **rht**-MOF-2,-3,-4a and descriptions are presented in the Supporting Information, as well as inelastic neutron scattering data. The pore size distribution for each shows the anticipated three different

pore sizes with the expected pore diameters in the mesoporous domain for the expanded **rht**-MOFs. The values for the exemplary trefoil-based **rht**-MOF-4a (7.2, 8.2, and 18.0 Å) deviate slightly from the calculated dimensions of the cavities from the crystal structure. This phenomenon is attributed to the inbuilt flexibility of the framework and reflected in the isotherm, which exhibits an additional continuous uptake starting at relatively low pressures with noticeable hysteresis. To confirm this unique “breathing” behavior, we performed CO₂ sorption at high pressures.^[15] The flexibility indeed manifests in the isotherm, which shows a multistep uptake behavior (Figure 4). In fact, it is apparent that additional accessible volume is generated at higher pressures (28 bar and 273 K), and the total volumetric uptake approaches the expected value (1.1 cm³ g⁻¹) calculated from the original crystal structure.

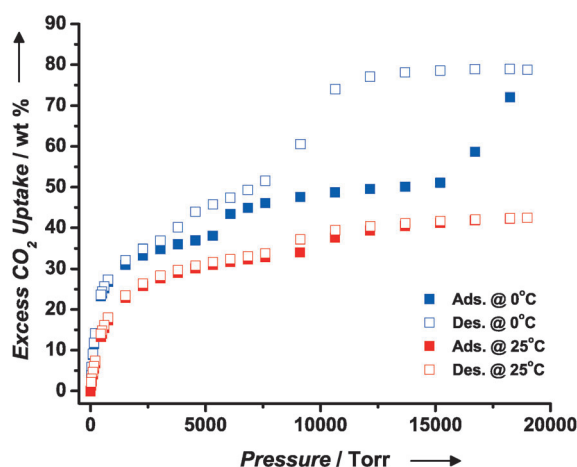


Figure 4. CO₂ high-pressure sorption isotherms for **rht**-MOF-4a.

In conclusion, we have described the design, synthesis, and facile tuning of the **rht**-MOF platform by way of expansion of the SBB, substitution of the triangular MBB, spacing of the distance between SBB and triangular MBB, introduction of various metals, and pre-synthesis functionalization. The robust **rht**-MOFs with accessible cavities in the micro-mesoporous range and 3D interconnecting channels, remain open (no interpenetration) along with some of the lowest reported crystalline framework densities and free volumes, significant porosities, and observable differences in H₂ uptake and energetics depending on framework composition, pore size, and functionality. The demonstration that numerous **rht**-MOFs can readily be targeted and synthesized from a variety of judiciously selected or designed ligands reveals a direct pathway to specific functional solid-state materials. The controlled production of a single product and the broad application scope of this synthetic method heralds a new era in functional materials design.

Experimental Section

Conditions and crystal data for the MOFs presented herein:

rht-MOF-2: Cu(NO₃)₂·2.5H₂O (29 mg), H₃L2 (11 mg), and DMF (1 mL), added to 20 mL vial, heated to 80°C/40 h to give blue-green polyhedral crystals. *Fm* $\bar{3}$ *m*, *a* = 63.931 Å.

rht-MOF-3: Cu(NO₃)₂·2.5H₂O (39 mg), H₃L3 (35 mg), and DMF (1 mL) added to 20 mL vial, heated to 75°C/40 h to give blue polyhedral crystals. *Fm* $\bar{3}$ *m*, *a* = 54.389.

rht-MOF-4a: Cu(NO₃)₂·2.5H₂O (20 mg), H₆L1 (37 mg), DMF (1 mL), and H₂O (1 mL) added to 20 mL vial, heated to 85°C/12 h, 105°C/23 h, 115°C/23 h to give green polyhedral crystals. *Fm* $\bar{3}$, *a* = 41.479 Å.

rht-MOF-4b: Zn(NO₃)₂·6H₂O (12 mg), H₆L1 (18 mg), DMF (1 mL), and NMP (1 mL) added to 20 mL vial, heated to 85°C/12 h to give colorless polyhedral crystals. *I4**m*, *a* = 29.3026 Å, *c* = 41.672 Å.

rht-MOF-4c: Co(NO₃)₂·6H₂O (24 mg), H₆L1 (37 mg), DMF (1 mL), and NMP (0.5 mL) added to 20 mL vial, heated to 85°C/12 h, 105°C/23 h to give a few red cube crystals. *I4**m*, *a* = 29.395 Å, *c* = 41.638 Å.

rht-MOF-5: Zn(NO₃)₂·6H₂O (12 mg), H₆L2 (27 mg), DMF (1 mL) and NMP (1 mL) added to 20 mL vial, heated to 85°C/12 h, 105°C/23 h to give a few orange cube crystals. *Fm* $\bar{3}$, *a* = 56.798 Å.

rht-MOF-6: H₆L3 (20 mg), Cu(BF₄)₂·6H₂O (15 mg), DMF (2 mL), HNO₃ (0.2 mL, 3.5 M in DMF) added to 20 mL vial, heated at 65°C/3d to yield a few green-blue block crystals. *Fm* $\bar{3}$ *m*, *a* = 68.604 Å.

rht-MOF-8: Cu(NO₃)₂·2.5H₂O (39 mg), H₃L4 (40 mg), DMF (1 mL) added to 20 mL vial, heated to 75°C/20 h, 85°C/12 h to give blue polyhedral crystals. *I4**m*, *a* = 41.557, *c* = 59.003 Å.

CCDC 866709 (**rht**-MOF-2), 866710 (**rht**-MOF-3), **rht**-MOF-4a (866711), 866712 (**rht**-MOF-4b), 866713 (**rht**-MOF-4c), 866714 (**rht**-MOF-5), 866715 (**rht**-MOF-6), and 884451 (**rht**-MOF-8) 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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