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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

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To cite this Article Hoffart, Dennis J. and Loeb, Stephen J.(2007) 'The Missing Link: A 2D Metal-Organic Rotaxane Framework (MORF) with One Rotaxane Linker and One Naked Linker', *Supramolecular Chemistry*, 19: 1, 89 – 93

To link to this Article: DOI: 10.1080/10610270600979165

URL: <http://dx.doi.org/10.1080/10610270600979165>

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The Missing Link: A 2D Metal–Organic Rotaxane Framework (MORF) with One Rotaxane Linker and One Naked Linker

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Received (in Southampton, UK) 14 July 2006; Accepted 5 August 2006

The [2]pseudorotaxane formed between the dicationic axle 1,2-bis-(4,4'-bipyridinium-mono-*N*-oxide)ethane and dibenzo-24-crown-8 ether (DB24C8) can act as a bridging ligand between metal centers to form metal organic rotaxane frameworks (MORFs). When cadmium(II) is used as the metal center the resulting structure is a network in which two [2]pseudorotaxanes, two 'naked' axles and two triflate anions coordinate to the Cd(II) center in a *trans*,-*trans*,-*trans*-arrangement. The two different linking ligands form a 2D 'square' net with only one direction comprised of rotaxanes. These nets layer in an A–B–A–B fashion with the crown ether units of one layer blocking the openings of the next layer to eliminate the formation of channels.

Keywords: Nitrogen ligands; Self-assembly; Coordination polymer; Metal organic framework; Rotaxane

INTRODUCTION

Mechanically interlocked molecules are well suited for the construction of molecular machines and solution studies on the dynamic nature and switching properties of these systems have generated a great deal of fundamental knowledge about the manipulation of nanoscale components [1–4]. Despite these advances, higher degrees of ordering are required to take advantage of the functional components and make them individually addressable and controllable [5,6].

Recently, we have investigated a strategy that involves ordering mechanically linked units in the solid state by incorporating them into metal-based polyrotaxanes, which we term metal-organic rotaxane frameworks (MORFs) [7]. This use of rotaxanes as linkers in metal–ligand self-assembly reactions

satisfies one of the fundamental requirements for the eventual organization of molecular machines into 1D, 2D or 3D frameworks [8,9]. In addition, since the rotaxane linker can be modified by retaining the bridging axle unit and exchanging the wheel component, this offers a very flexible methodology for supramolecular modification that can potentially be used to tune the internal properties of these materials.

To date, we have reported the successful preparation and characterization of 1D and 2D MORFs incorporating the [2]pseudorotaxane ligand [1 C DB24C8]²⁺ (1²⁺ = 1,2-bis(4,4'-bipyridinium)ethane; DB24C8 = dibenzo-24-crown-8 ether) with first row transition metals. Co(II) and Zn(II) gave 1D MORFs while, under different crystallization conditions, Co(II), Ni(II), Cu(II) and Cd(II) ions gave isomorphous 2D square networks with large open channels [4]. We were unable to obtain 3D MORFs using transition metals and [1 C DB24C8]²⁺ and rationalized that our failure was due to the steric problems associated with trying to coordinate six very bulky [2]pseudorotaxanes to the same metal ion in an octahedral geometry. In order to relieve this steric problem we changed two parameters. We extended the length of the linker by converting the pyridine ligands to *N*-oxides to give [2 C DB24C8]²⁺ (2²⁺ = 1,2-bis-(4,4'-bipyridinium-mono-*N*-oxide)ethane) and employed larger lanthanide ions that are more oxophilic and prefer higher coordination numbers. The coordination polymers formed with the Ln ions, Sm(III), Eu(III), Gd(III) or Yb(III) and [2 C DB24C8]²⁺ were indeed 3D MORFs in which each metal ion coordinated six [2]pseudorotaxane ligands [5] (Fig. 1).

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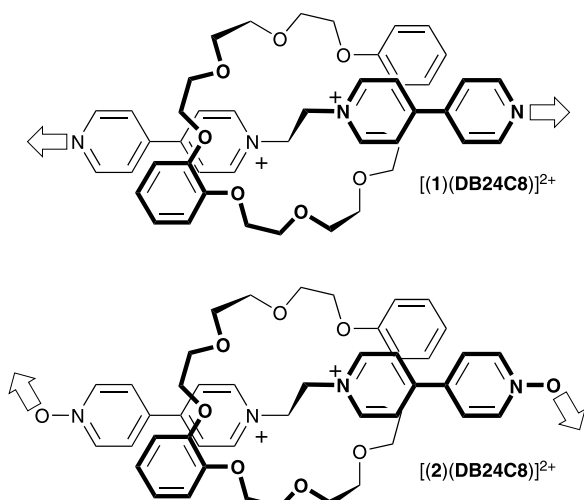
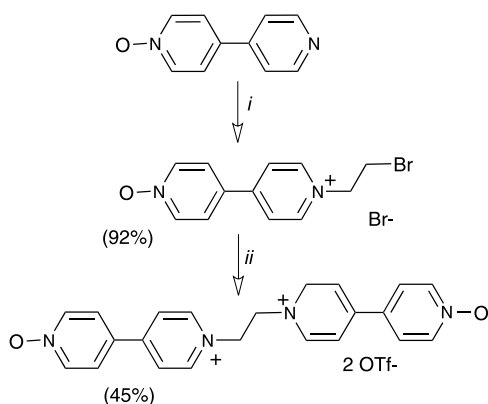


FIGURE 1 The [2]pseudorotaxanes $[1 \subset \text{DB24C8}]^{2+}$ and $[2 \subset \text{DB24C8}]^{2+}$ (both as the CF_3SO_3 salts) can act as bridging linkers between metal centers to form metal-organic rotaxane frameworks (MORFs).

Herein, we pose the question; what would happen if we incorporated the longer *N*-oxide linking [2]pseudorotaxane $[2 \subset \text{DB24C8}]^{2+}$ but still utilized a smaller transition metal ion like Cd(II)? The answer is we get a completely new and unexpected result. The Cd(II) ions retain an octahedral geometry and the resulting network is a 2D MORF but only one of the linking axles contains a DB24C8 wheel (is a rotaxane); the other is *missing* its crown ether and is 'naked'.

RESULTS AND DISCUSSIONS

The pyridine-*N*-oxide terminated axle 2^{2+} was prepared as the triflate salt in three steps as outlined in Scheme 1. The mono-*N*-oxide of 4,4'-bipyridine was prepared by the literature method and then reacted with dibromoethane to give the intermediate



SCHEME 1 Reagents and conditions: *i*, $\text{BrCH}_2\text{CH}_2\text{Br}$ in $\text{CHCl}_3/\text{MeCN}$ (1:1) reflux 24 h; *ii* 4,4'-bipyridinium-*N*-monoxide in MeCN reflux for 1 week then anion exchanged with $[\text{Na}][\text{OTf}]$ (aq).

product bromoethyl-4,4'-bipyridinium-*N*-monoxide as the bromide salt [10]. This material was further alkylated with another equivalent of 4,4'-bipyridinium-*N*-monoxide and then anion exchanged to yield $[2][\text{OTf}]_2$ [11].

The new MORF material was prepared by combining one equivalent of $[2][\text{OTf}]_2$ with three equivalents of DB24C8 in MeNO₂ and then adding this solution to a solution of $[\text{Cd}][\text{OTf}]_2$ in MeNO₂. X-ray quality crystals were grown by allowing isopropyl ether to slowly diffuse into the reaction mixture. The initial crop of crystals produced a 30% yield and was used for all analyses; subsequent collections resulted in a combined yield that was essentially quantitative. The only side-product observed was the excess DB24C8 used in the reaction; traces of this neutral organic compound were easily removed by washing with a non-polar solvent such as toluene.

The X-ray crystal structure of this new MORF material shows that the solid has the formulation $\{[\text{Cd}(2 \subset \text{DB24C8})(2)(\text{OTf})_2][\text{OTf}]_4(\text{CH}_3\text{NO}_2)_4\}_n$. The Cd(II) metal centers adopt an octahedral geometry with three different pairs of ligands in an all trans arrangement. Two pseudorotaxane ligands, $[2 \subset \text{DB24C8}]^{2+}$ and two naked axles, $[2]^{2+}$ define a square plane while two triflate anions are in the axial positions (see Fig. 2). Since the *N*-oxide terminated axles can bridge two metal ions, these ligands bridge Cd(II) ions to yield a 2D 'square' grid (Fig. 3). This is reminiscent of the Cd(II) MORF prepared using the pyridine-based [2]pseudorotaxane ligand $[1 \subset \text{DB24C8}]^{2+}$. In that structure, the cavities of the grid were aligned to produce large channels filled with solvent [4]. However in the present structure, each cavity is filled by crown ethers from the layers above and below. This A–B–A–B layering pattern can be clearly seen in Fig. 4.

The network is actually more reminiscent of the 1D MORF structure based on Co(II) or Zn(II) and $[1 \subset \text{DB24C8}]^{2+}$ as it can be thought of as a pillared 1D polyrotaxane [4]. That is, the two *trans* oriented [2]rotaxanes coordinate to the Cd(II) center in 1D while the two 'naked' threads *cis* to each [2]rotaxane unit pillar the polyrotaxane strands in the second dimension. Figure 5 shows this pillaring viewed down the 1D polyrotaxane axis.

Obviously, the increased length of $[2 \subset \text{DB24C8}]^{2+}$ versus $[1 \subset \text{DB24C8}]^{2+}$ has had a significant effect on the topology of the MORF created. In this new MORF, the individual nets pack with the crown ether of one layer filling the void space in an adjacent layer. This 'nesting' of one crown ether into the cavity of an adjacent layer can only occur if the cavity is large enough. The increased length of the axle allows for this possibility and the combination of rotaxane and naked axle linkers appears to create the ideal sized cavity for the observed layering motif. This is most

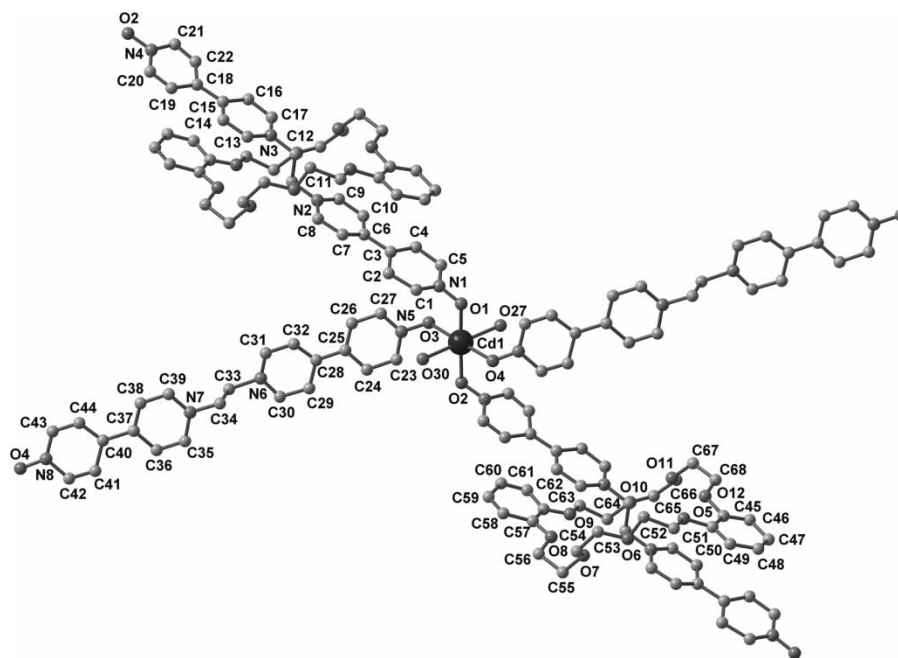


FIGURE 2 X-ray structure of the 2D coordination polymer (MORF) $[[\text{Cd}(\text{2-DB24C8})(\text{OTf})_2][\text{OTf}]_4(\text{CH}_3\text{NO}_2)_4]_n$ showing the coordination sphere around Cd(1). The numbering scheme is shown; two of the CF_3SO_3 anions are coordinated to the metal center but only the oxygen atoms O(27) and O(30) are shown for clarity. Selected distances (Å) and angles ($^\circ$): Cd(1)–O(1) 2.202(12), Cd(1)–O(2) 2.281(14), Cd(1)–O(3) 2.312(11), Cd(1)–O(4) 2.261(13), Cd(1)–O(27) 2.297(11), Cd(1)–O(30) 2.293(11), O(1)–Cd(1)–O(2) 178.2(6), O(1)–Cd(1)–O(3) 93.6(4), O(1)–Cd(1)–O(4) 86.1(5), O(1)–Cd(1)–O(27) 89.6(5), O(1)–Cd(1)–O(30) 88.5(5), O(2)–Cd(1)–O(3) 88.1(4), O(2)–Cd(1)–O(4) 92.2(5), O(2)–Cd(1)–O(27) 89.8(5), O(2)–Cd(1)–O(30) 92.1(6), O(3)–Cd(1)–O(4) 178.6(6), O(3)–Cd(1)–O(27) 93.8(4), O(3)–Cd(1)–O(30) 89.5(5), O(4)–Cd(1)–O(27) 84.8(5), O(4)–Cd(1)–O(30) 91.9(6), O(27)–Cd(1)–O(30) 176.3(8), Cd(1)–Cd(1) $'$ 22.51(1), Cd(1)–Cd(1) $''$ 22.77(1).

likely the driving force behind the creation of a 2D MORF with a combination of rotaxane and naked axle bridging ligands and may be a templating effect that can be utilized in future MORF design.

Finally, a property of this new MORF that is intriguing is its crystallization in the non-centrosymmetric space group, P1. All the crown ether wheels are oriented in the same fashion along each strand of each grid, see Figs. 3 and 4. This may be significant as it should be possible to exchange **DB24C8** with an

unsymmetrically substituted crown ether and thus orient all the wheel dipoles in the same direction by virtue of their entrapment on the metal-ligand grid. This has potential as a novel method for creating non-linear optical (NLO) materials by supramolecular modification.

In conclusion, it appears that it is not only possible to design and prepare what we might call saturated MORFs in which every bridging ligand is a rotaxane, but also MORFs that are polyrotaxanes connected or

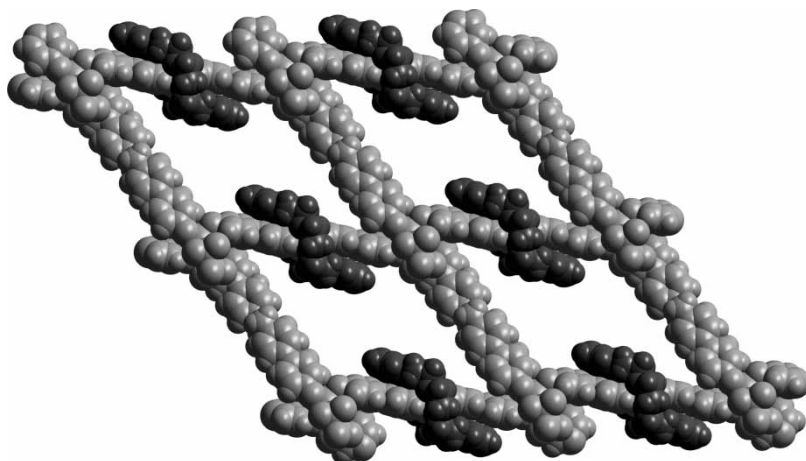


FIGURE 3 X-ray structure of the 2D MORF showing one layer in space-filling mode. Note that the axes in one direction are threaded through molecules of **DB24C8** to give a 1D polyrotaxane type structure while the axes in the other direction are naked (i.e. do not thread through a crown ether).

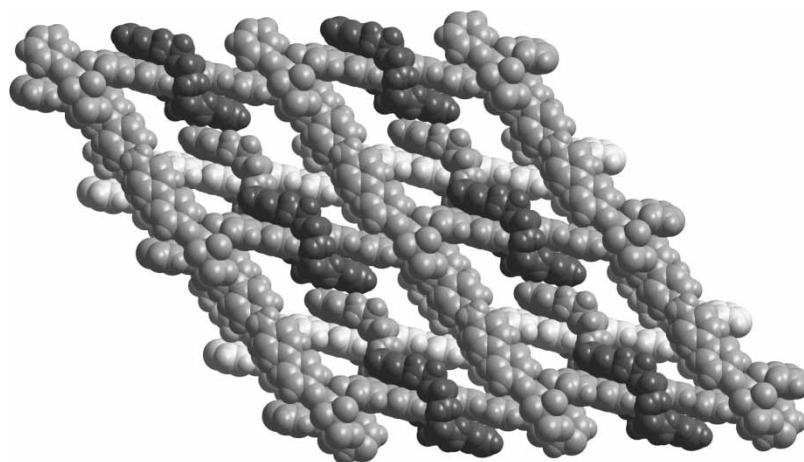


FIGURE 4 X-ray structure of the 2D MORF showing two adjacent layers in space-filling mode. Note how the two layers are offset so that the DB24C8 molecules from one layer sit directly over the cavities of the next layer eliminating any porosity.

pillared into a higher dimensional solid by more standard non-rotaxane ligands. Current work is focused on this methodology to prepare MORFs with predictable dimensionality and positioned dynamic components.

EXPERIMENTAL

Preparation of Bromoethyl-4,4'-Bipyridinium-*N*-Monoxide Bromide

4,4'-Bipyridinium-*N*-monoxide (5.00 g, 29.0 mmol) was dissolved in a 1:1 CHCl₃:MeCN solution (10 mL) and this mixture added to neat 1,2-dibromoethane (40 mL). The reaction was then refluxed for 24 h. The solution was filtered hot and the isolated brown precipitate washed with CHCl₃ and dried in air at room temperature. Yield 9.60 g (92%). ¹H NMR (δ, ppm, D₂O): H_a 8.928 (d, 2H, ³J_{ab} = 6.9 Hz), H_b 8.363 (d, 2H, ³J_{ab} = 6.9 Hz), H_c 8.439 (d, 2H, ³J_{cd} = 7.9 Hz), H_d 8.046 (d, 2H, ³J_{cd} = 7.9 Hz), H_e 4.992 (t, 2H, ³J_{ef} = 5.8 Hz), H_f 3.930 (t, 2H, ³J_{ef} = 5.8 Hz) (see Fig. 6).

Preparation of Bis-(4,4'-Bipyridinium-*N*-Monoxide)Ethane Triflate, [2][OTf]₂

Bromoethyl-4,4'-bipyridinium-*N*-monoxide bromide, prepared as described above (5.00 g, 13.9 mmol), and 4,4'-bipyridinium-*N*-monoxide (3.59 g, 20.9 mmol) were dissolved in MeCN (75 mL) and refluxed for 1 week. The light brown precipitate formed was filtered, dried and then dissolved in a minimum amount of water. Five equivalents of [Na][OTf] were added and the mixture was heated until the solution was homogeneous. The solution was then cooled and the triflate salt of 2²⁺ isolated as an off-white powder. Yield 4.23 g (45%). ¹H NMR (δ, ppm, CD₃NO₂): H_a 8.892 (d, 4H, ³J_{ab} = 6.9 Hz), H_b 8.449 (d, 4H, ³J_{ab} = 6.9 Hz), H_c 8.305 (d, 4H, ³J_{cd} = 7.4 Hz), H_d 7.965 (d, 4H, ³J_{cd} = 7.4 Hz), H_e 5.417 (s, 4H) (see Fig. 6).

Formation of the Metal Organic Rotaxane Framework (MORF) Material

[2][OTf]₂ (15 mg, 0.02 mmol) and DB24C8 (30 mg, 0.06 mmol) were combined in MeNO₂ (0.5 mL).

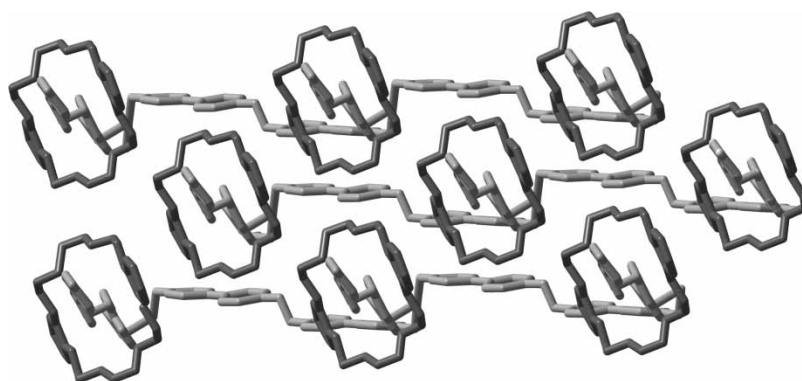


FIGURE 5 A view of the X-ray structure of the 2D MORF looking down the polyrotaxane axle. Note the resemblance to a pillared 1D MORF.

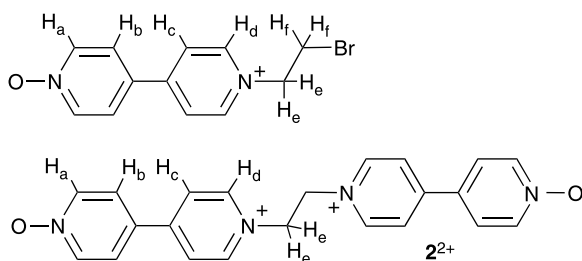


FIGURE 6 The numbering schemes for the ^1H NMR spectra of the bromoethylbipyridinium-*N*-monoxide cation and $[2][\text{OTf}]_2$.

TABLE I X-ray crystallographic data collection, solution and refinement parameters for $[\text{Cd}(2\text{CDB24C8})(2)(\text{OTf})_2][\text{OTf}]_4(\text{CH}_3\text{NO}_2)_n$

CCDC number [†]	617324
Empirical formula	$\text{C}_{78}\text{H}_{84}\text{CdF}_{18}\text{N}_{12}\text{O}_{38}\text{S}_6$
Formula weight	2444.33
Crystal description	Yellow–orange blocks
Crystal size (mm)	$0.32 \times 0.24 \times 0.24$
Crystal system	Triclinic
Space group	P1 (No. 1)
<i>a</i> (Å)	11.579(1)
<i>b</i> (Å)	12.459(1)
<i>c</i> (Å)	19.000(2)
α (°)	88.380(2)
β (°)	84.943(2)
γ (°)	65.788(2)
<i>Z</i>	1
Cell volume (Å ³)	2490.2(4)
Density calculated (g cm ⁻³)	1.630
μ (mm ⁻¹)	0.471
Independent reflections (<i>R</i> _{int})	19929 (0.0396)
Data/restraints/parameters	16828/342/1375
Goodness-of-fit on <i>F</i> ²	1.011
Final <i>R</i> 1 [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0844
Final <i>wR</i> 2 [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.1910
Final <i>R</i> 1 (all data)	0.1617
Final <i>wR</i> 2 (all data)	0.2397
Residuals peak/hole (e/Å ³)	1.439/−1.031

[†]Data for this compound can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

This solution was then added to a solution of $[\text{Cd}^{\text{II}}][\text{OTf}]_2$ (4 mg, 0.01 mmol) in MeNO_2 (0.5 mL). *iso*-Propylether vapour was allowed to diffuse into the reaction mixture to produce orange, X-ray quality crystals. Yield 8.4 mg (30%).

General X-ray Diffraction

All data were collected on a Brüker SMART CCD instrument at room temperature. Reflection data

were integrated from frame data obtained from a hemisphere. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with the assigned space group. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the datasets. The structure was solved by direct methods, completed by subsequent Fourier synthesis and refined with full-matrix least squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All structural drawings were created using the program DIAMOND [12]. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library [13]. A summary of the details of all X-ray data collection, solution and refinement parameters are listed in Table I.

Acknowledgements

SJL thanks the Natural Sciences and Engineering Council of Canada for financial support for this research.

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