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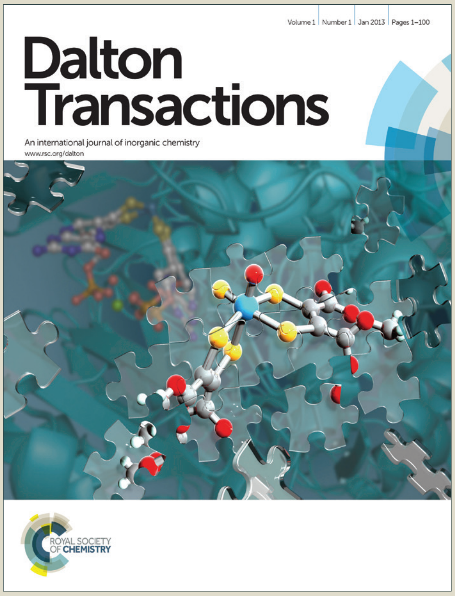

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ARTICLE TYPE

Rhenium(I)-based bridgeless double metallocalix[4]arenes

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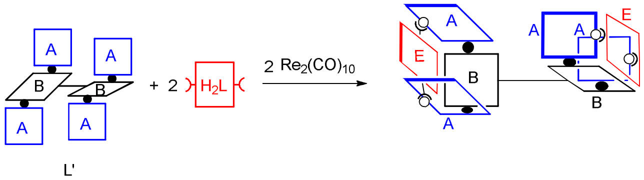
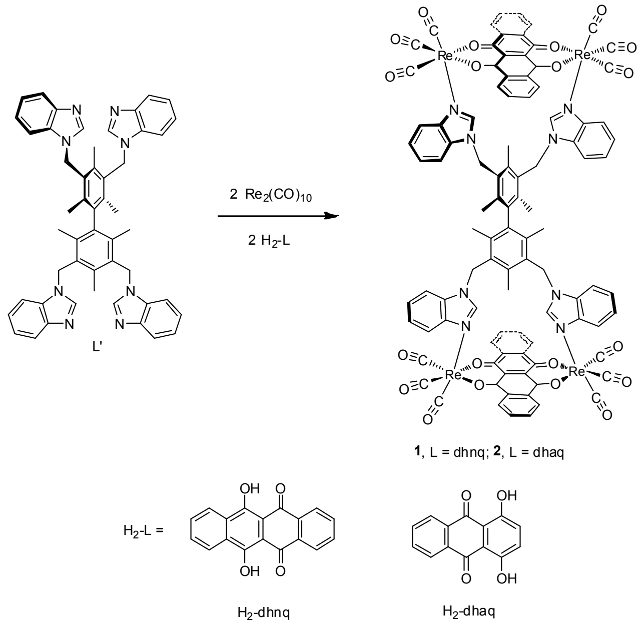
Bridgeless double metallocalix[4]arenes possessing orthogonally arranged two dinuclear cavitands were obtained from a $Re_2(CO)_{10}$, rigid bis-chelating OO donors (H_2-L), and a flexible bis-ditopic NN donors (L′) in a one-pot approach.

The design and synthesis of calix[4]arene type metallocavitands consist of alternatively arranged four rigid walls and four metal ions/two metal ions and two methylene units have been getting continuous research interest because of their potential applications in molecular sensors, catalysis, unique regioselective reactivity, and enantioselective guest recognition.[1-6] Among the known design principles for various shapes and sizes of metallocavitands, the combination of a $Re_2(CO)_{10}$, rigid bis-chelating O donor, and flexible benzimidazolyl N donor possessing phenylene(CH_2-benzimidazolyl)$_n$ (n = 2,3) core is one of the simple and successful routes to neutral heteroleptic dinuclear metallocalix[4]arenes.[6a-d] Up to now, most studies in metallocavitands are centred on dinuclear monocyclic metallocalix[4]arenes. Because of their importance in various fields, efforts are being directed toward the synthesis of bis-/tris- and multi-metallocavitands, in which cavitands are arranged either linearly or spherically.[6d-6g] The multicavitands are expected to amplify the receptor or physio-chemical properties of the individual components if their proximate cavities may interact synergistically.[7] Herein, we report the first design principle i.e. a combination of two $Re_2(CO)_{10}$, two rigid bis-chelating OO donors, and a flexible bis-ditopic NN donors, for a bridgeless double metallocalix[4]arenes, in which dinuclear metallocavitand pairs directly connected through phenylene carbon atoms (Scheme 1).



Scheme 1 Approach to bridgeless double metallocalix[4]arenes-shaped metallocavitand. A = benzimidazolyl; B = phenylene; H_2L = bis-chelating unit; • = CH_2; o = *fac*–$Re(CO)_3$.

The solvothermal treatment of a $Re_2(CO)_{10}$, H_2L (H_2L = 6,11-dihydroxy-5,12-naphthacenedione, H_2-dhnq or 1,4-dihydroxy-9,10-anthraquinone, H_2-dhaq) and neutral L′ in toluene resulted in the formation of complexes **1** and **2** ($[\{(CO)_3Re(\mu{-}L)Re(CO)_3\}_2(\mu{-}L')]$; **1**, L = dhnq and **2**, L = dhaq) (Scheme 2).‡ The products are air and moisture stable and sparingly soluble in polar organic solvents. The Fourier transform infrared spectrum of complex **1** showed three strong bands at 2017, 1899, and 1881 cm^{-1}, characteristic of *fac*-$Re(CO)_3$ unit in an asymmetric environment.[8] The X-ray photoelectron spectroscopy spectra of **1** and **2** displayed $Re4f_{7/2}$ and $Re4f_{5/2}$ peaks (Fig. S1-S2 in ESI†), indicating the +1 oxidation state for rhenium. [6g] . The eletrospray ionization mass spectrometry (ESI-MS) spectra of compounds showed a molecular-ion (m/z = 2416.2473 for $[\mathbf{1}]^+$, and 2317.2050 for $[\mathbf{2}+H]^+$), with the isotope pattern matching the theoretical values (Fig.1 and Fig. S3-S4 in ESI†). The ligand L′ was synthesized by treating 3,3′,5,5′-tetrakis(bromomethyl)2,2′,4,4′,6,6′-hexamethylbiphenyl with benzimidazole in the presence of NaH using the known procedure as that for imidazolyl-based N donor.[9] A single set of proton signals with 8:20 methylene proton to benzimidazolyl proton ratio confirmed the formation of the ligand. The ESI-MS of L′ showed molecular-ion peak (m/z = 759.3891 for $[L+H]^+$) (Fig. S5-S8, ESI†).



Scheme 2 Synthesis of **1** and **2**.

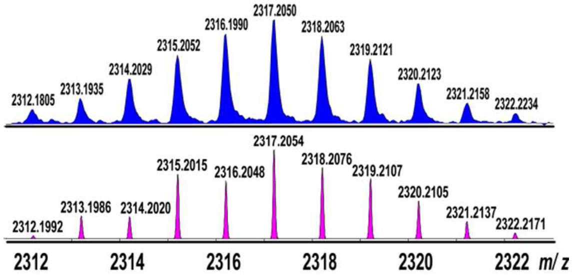


Fig. 1 Experimental (top) and calculated (botton) ESI-TOF-MS spectra of $[\mathbf{2}+H]^+$.

The result of a single-crystal X-ray study of **1** showed that complex adopts a M_4L_2L'-type supramolecular coordination complex architecture which is made up of four *fac*-$Re(CO)_3$ cores, two $dhnq^{2-}$, and one L (Fig. 2). Complex **1** is best regarded as a *bridgeless double metallocalix[4]arenes* i.e. two metallocalix[4]arene units connected through the aromatic-aromatic bond. Each metallocavitand consists of two *fac*-$Re(CO)_3$ cores, one $dhnq^{2-}$, phenylene(CH_2-benzimidazolyl)$_2$ unit, and methyl group ({··Re1···dhnq···Re2···benzimidazolyl–C^1H_2–*meta*-phenylene–C^2H_2–benzimidazolyl··}, nonbonding distances of Re1···Re2, Re1···C^1H_2, C^1H_2···C^2H_2, and C^2H_2···Re2 are 8.579, 5.586, 5.071, and 5.617 Å). The size of the upper rim of each cavitand including the van der Waals radii are ~5.49-7.50 Å (benzimidazolyl···benzimidazolyl), ~8.34 Å (dhnq···*H*-CH_2-phenylene), and ~5.58 Å (depth). These values are comparable to the organic calix[4]arene framework.[5] A similar type of cavitand ([{$(CO)_3Re(\mu$–dhnq)$Re(CO)_3$}(μ–L″)] (**I**), where L″ = 1,3,5-tris(2-(methylthio)benzimidazol-1-ylmethyl)2,4,6-trimethylbenzene) was found in the monocyclic metallocalix[4]arene.[6b] Two metallocavitands in **1** are connected together by *para-para* biphenylene linkage similar to the bridgeless 5,5′-bicalix[4]arene.[7] However, the two metallocavitand cavities are arranged orthogonal to each other, dihedral angle of biphenylene unit is 88°. The overall size of **1** is ~ 22 × 13 × ~11 Å.

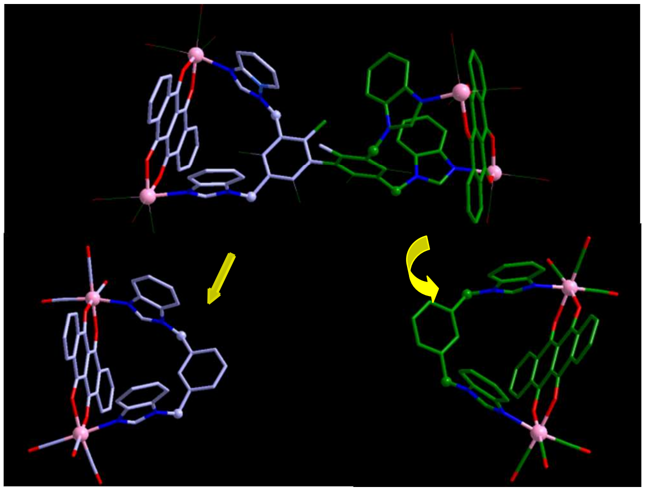


Fig. 2 Molecular structure of **1**. Top: Each metallocalix[4]arene units shown as thick stick model with different colour. Bottom: Two cavitands shown separately by disconnecting Ar–Ar bond; left and right, metallocalix[4]arene framework as such and after ~90° rotation. Light blue = green = C, blue = N, red = O, and rose = Re.

In **1**, rhenium adopts a distorted octahedral geometry with C_3NO_2 donor environment. The dhnq chelated with two rhenium atoms symmetrically through the four oxygen atoms. The electrons in the dhnq are confined to the two chelating units and two terminal arene units.[10] The tetratopic ligand acts as two *syn*-bis(bidentate) nitrogen donors. The Re–C(C≡O) bond lengths in **1** are in the ranges 1.15–1.19 Å, which are commonly observed in the related tricarbonyl rhenium complexes.[8] The C≡O bond lengths *trans* to the benzimidazolyl and *trans* to the $dhnq^{2-}$ units are similar.

A strong intramolecular C–H···π interactions found between the hydrogen atom of 2-methyl and the dhnq unit (C15(CH_3)···C36/C41(dhnq) = 3.6383/3.5817Å). The crystal structure of **1** is further stabilized by nonclassical hydrogen bonding interactions Re–C≡O(4)···H–C16 (*d* = 2.485 Å, angle = 152°), π···π (dhnq···dhnq = 3.6489 Å), and C–H···π interactions(Fig. S10-S12, ESI†).

Though the quality of the diffraction data of complex **2** is poor, the bridgeless double metallocalix[4]arenes framework structure was confirmed without any doubt. The structure of 2 is similar to those of complex **1**. However, the size of the two metallocavitands is varied in **2** due to the different size and arrangement of the dhaq units. Due to the poor diffraction data of **2**, further structural discussion of metallocalix[4]arene is limited.

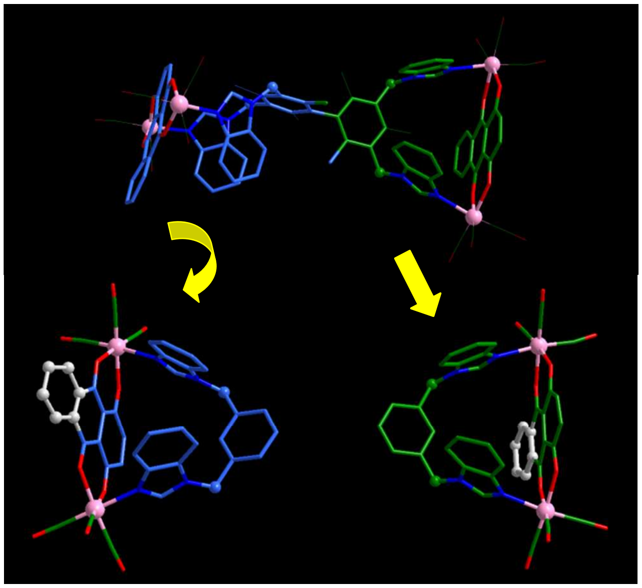


Fig. 3 Molecular structure of **2**. Top: Each metallocalix[4]arene units shown as thick stick model with different colour. Bottom: Two cavitands shown separately by disconnecting Ar–Ar bond; left and right, metallocalix[4]arene framework as such and after ~90° rotation. Blue = green = gray = C, dark blue = N, red = O, and rose = Re.

The UV-visible absorption spectra of **1** and **2** in DMF (Fig. S14-S15, ESI†) contain intense absorptions between 250-290 nm for **1**, and 220-280 nm for **2**, which are assigned to π→π* transitions. Some intraligand charge transfer (ILCT) transition is also possible in the region. The broad absorption with band maxima at ~387 nm for **1**, and 412 nm for **2** may be assigned to both ILCT and metal–to–ligand charge transfer (MLCT) transitions based on the previous literature reports on mononuclear metallocalix[4]arene **I** and related cavitands.[8] The lower energy absorption with band maxima 568 and 612 nm for **1**, and 607 and 650 nm for **2** may be assigned to the excitation of the quinonoid moiety with some contributions from the MLCT transitions.[8b]

Conclusions

A new type of metallocavitands similar to bridgeless biscalix[4]arenes was synthesized using newly synthesized neutral, flexible, and bis-ditopoic benzimidazolyl N donor, bis-chelating ligands, and a $Re_2(CO)_{10}$ by solvothermal method. The tetranuclear supramolecules are neutral and consist of two dinuclear metallocalix[4]arene cavitands. To the best of our knowledge, this is the first report of the bridgeless biscalix[4]arene-shaped metallocavitands. The study provides a way to assemble metallocavitands, particularly double metallocavitands with a tuneable framework and cavity via a simple one-step synthetic approach.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section for L′ and various spectra and data of L′, **1** and **2**; Crystallographic data of **1** (CCDC 1051408). For ESI and crystal data table see DOI: 10.1039/b000000x/.

‡ Synthesis of $[\{(CO)_3Re(\mu\text{–dhnq})Re(CO)_3\}_2(\mu\text{–L}')]$ (**1**). A mixture of $Re_2(CO)_{10}$ (100 mg, 0.1532 mmol), H_2-dhnq (44.46 mg, 0.1532 mmol), and L (58.1 mg, 0.0766 mmol) in toluene (10 mL) in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 48 h and then cooled to 25 °C. Good quality, orange-red crystals were obtained and separated by filtration. Yield: 85 % (157 mg, weight of crystals). Anal. Calcd for $C_{98}H_{62}N_8O_{20}Re_4$: C, 48.71; H, 2.59; N, 4.64. Found: C, 48.79; H, 2.65; N, 4.61. FT-IR (KBr, cm^{-1}): 2017, 1899, 1881 (C≡O).

‡Synthesis of $[\{(CO)_3Re(\mu\text{–dhaq})Re(CO)_3\}_2(\mu\text{–L}')]$ (**2**). Dark-green crystals were obtained by following a similar procedure to that for **1** using $Re_2(CO)_{10}$ (100.5 mg, 0.154 mmol), H_2-dhaq (37.1 mg, 0.1544 mmol), L (58.3 mg, 0.0768 mmol), toluene (10 mL), and acetone (5 mL). Yield: 45 % (103.7 mg, weight of crystals). The crystals were crushed into powder and washed with hexane several times. The final powder was kept in an oven at 65° C over 12 h. Anal. Calcd for $C_{90}H_{58}N_8O_{20}Re_4$: C, 46.67; H, 2.52; N, 4.84. Found: C, 46.53; H, 2.48; N, 4.72. FT-IR (KBr, cm^{-1}): 2012, 1899, 1878 (C≡O).

1. P. D. Frischmann and M. J. MacLachlan, *Chem. Soc. Rev*., 2013, **42**, 871 and references therein.
2. (a) B. Lippert and P. J. Sanz Miguel, *Chem. Soc. Rev*., 2011, **40**, 4475 and references therein; (b) J. Kulesza, B. S. Barros and S. A. Junior, *Coord. Chem. Rev.*, 2013, **257**, 2192.
3. (a) E. Barea, J. A. R. Navarro, J. M. Salas, M. Quiros, M. Willermann and B. Lippert, *Chem. Eur. J.,* 2003, **9**, 4414; (b) M. Maekawa, H. Konaka, T. Minematsu, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *Chem. Commun.,* 2007, 5179; (c) E. G. Bardajı, E. Freisinger, B. Costisella, C. A. Schalley, W. Bruning, M. Sabat and B. Lippert, *Chem. Eur. J.,* 2007, **13**, 6019; (d) N. Das, P. J. Sanz Miguel, A. Khutia, M. Lazar and B. Lippert, *Dalton Trans.,* 2009, 9120; (e) M. A. Galindo, S. Galli, J. A. R. Navarro and M. Angustias Romero, *Dalton Trans.,* 2004, 2780; (f) E. Rufino-Felipe, M. A. Munoz-Hernandez , H. F. Saucedo-Azpeitia and S. A. Cortes-Llamas, *Inorg. Chem*., 2012, **51**, 12834.
4. (a) M. Yoshizawa, M. Tamura and M. Fujita, *Science,* 2006, **312**, 251; (b) D. M. Vriezema, M. C. Aragones, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan and R. J. M. Nolte, *Chem. Rev.,* 2005, **105**, 1445.
5. (a) C. D. Gutsche, Calixarenes, in: J. F. Stoddart (Ed.), Royal Society of Chemistry, Unicus Graphics Ltd., West Sussex, UK, 1992; (b) D. Coquiere, S. Le Gac, U. Darbost, O. Seneque, I. Jabin and O. Reinaud, *Org. Biomol. Chem.*, 2009, **7**, 2485 and references therein.
6. (a) P. Rajakannu, S. M. Mobin and M. Sathiyendiran, *J. Organomet. Chem.,* 2014, **771**, 68; (b) P. Rajakannu, P. Elumalai, B. Shankar, F. Hussain and M. Sathiyendiran, *Dalton Trans.,* 2013, **42**, 11359; (c) P. Rajakannu, P. Elumalai, S. M. Mobin, K. L. Lu and M. Sathiyendiran, *J. Organomet. Chem.,* 2013, **743**, 17; (d) P. Rajakannu, P. Elumalai, F. Hussain and M. Sathiyendiran, *J. Organomet. Chem.,* 2013, **725**, 1; (e) B. Shankar, F. Hussain and M. Sathiyendiran, *J. Organomet. Chem.,* 2012, **719**, 26; (f) B. Shankar, P. Elumalai, R. Shanmugam and M. Sathiyendiran, *J. Organomet. Chem.,* 2014, **749**, 22426; (g) B. Shankar, P. Elumalai, S. D. Sathiyashivan and M. Sathiyendiran, *Inorg. Chem*., 2014, **53**, 10018.
7. S. Sameni, C. Jeunesse, D. Matt and J. Harrowfield, *Chem. Soc. Rev.,* 2009, **38**, 2117.
8. (a) M. Sathiyendiran, J. Y. Wu, M. Velayudham, G. H. Lee, S. M. Peng and K. L. Lu, *Chem. Commun.,* 2009, 3795; (b) D. Bhattacharya, M. Sathiyendiran, J. Y. Wu, C. H. Chang, S. C. Huang, Y. L. Zeng, C. Y. Lin, P. Thanasekaran, B. C. Lin, C. P. Lin, C. P. Hsu, G. H. Lee, S. M. Peng and K. L. Lu, *Inorg. Chem.,* 2010, **49**, 10264; (c) P. Rajakannu, B. Shankar, A. Yadav, R. Shanmugam, D. Gupta, F. Hussain, C. H. Chang, M. Sathiyendiran and K. L. Lu, *Organometallics*, 2011, **30**, 3168.
9. (a) H. S. Weng, J. D. Lin, X. F. Long, Z. H. Li, P. Lin and S. W. Du, *J. Solid State Chem.,* 2009, **182**, 1408; (b) C. L. Chen, J. Y. Zhang and C. Y. Su, *Eur. J. Inorg. Chem*., 2007, 2997; (c) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim and H. C. Zur Loye, *J. Am. Chem. Soc*., 2003, **125**, 8595.
10. Y. F. Han, H. Li and G. X. Jin, *Chem. Commun.,* 2010, **46**, 6879.

Graphical contents entry

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Bridgeless double metallocalix[4]arenes possessing orthogonally arranged two dinuclear cavitands was obtained from a $Re_2(CO)_{10}$, rigid bis-chelating units, and flexible bis-ditopic N-donor in a one-pot approach.