Sathiyendiran, Malaichamy

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1 Inorganica Chimica Acta, 2027, 604, 123455

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Azolato and hydroxo-bridged dinuclear rhenium complexes as potent agents against triple-negative breast cancer

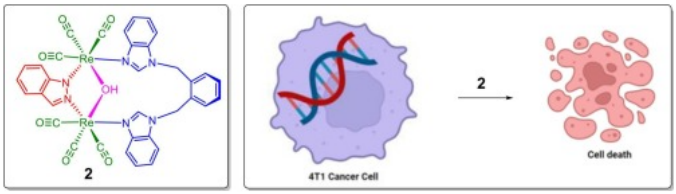
Upasana Phukon, Chandra Lekha Putta, Sajmina Khatun, Bhaskaran Shankar, ... Malaichamy Sathiyendiran

Article 123455

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J. Chem. Sci. (2026)138:65
https://doi.org/10.1007/s12039-026-02526-7

RESEARCH ARTICLE

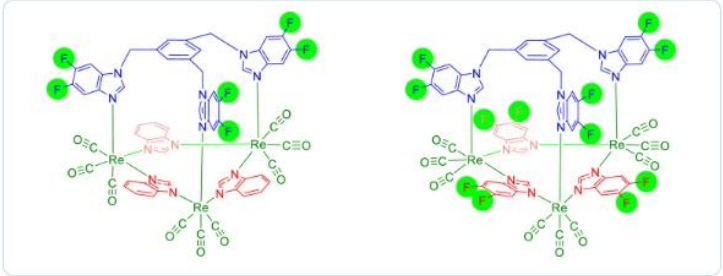
Self-assembly and structural characterization of fluorine-decorated rhenium(I) heteroleptic metallocages

BHARATHI BHANOTH, W KEERTHI, REEMA L BORKAR* and MALAICHAMY SATHIYENDIRAN*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
*Corresponding authors: 19chph19@uohyd.ac.in; msathi@uohyd.ac.in

Graphical abstract

A fluorinated tripodal ligand (L) was synthesized and used to construct two fluorinated Re(I) metallocages via a one-pot method. ATR-FTIR, ^{1}H NMR, and mass spectrometry confirmed their formation. Simple, symmetric NMR patterns with characteristic shifts confirmed coordination and the expected cage architecture.



3

Journal of Molecular Liquids 456 (2026) 129637

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Head-to-tail parallel stacking enhanced tautomer emission

Arup Das Kanungo [a], Krishna Prasad Ghanta [b], Ramesh Babu Yathirajula [d], Malaichamy Sathiyendiran [c], Parameswar Krishnan Iyer [a,d], G. Krishnamoorthy [a,*]

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[c] Department of Chemistry, University of Hyderabad, Hyderabad, Telangana, India
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ARTICLE INFO

Keywords:
ESIPT
Photoisomerisation
AIEE
Molecular dynamics
OLED

ABSTRACT

2,2′-(1,4-phenylenebis(1H-benzo[d]imidazole-1,2-diyl))diphenol (PBIDP) undergoes excited state intramolecular proton transfer (ESIPT). It emits triple emission in solution. The non-radiative photoisomerisation process of PBIDP results in a very low fluorescence quantum yield in solutions (0.07 in tetrahydrofuran (THF)). The photophysical characteristics of PBIDP in water-THF mixtures and in the solid state were investigated using UV–visible spectroscopy, steady-state, and time-resolved photoluminescence techniques. The molecule exhibits aggregation-induced emission enhancement (AIEE) in water-THF binary solvent mixture. Dynamic light scattering (DLS) and a field-emission scanning electron microscope (FESEM) were used to determine the size and shape of aggregated particles. The mechanism of AIEE was explored by the crystal structure, intra- and intermolecular noncovalent interactions (NCIs) analysis, and molecular dynamics simulation studies. PBIDP emits very strong emission in the solid state as compared to that in the liquid state, with a very high fluorescence quantum yield (0.59). Therefore, using PBIDP, an organic light-emitting diode (OLED) device was fabricated.

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Dalton Transactions

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PAPER

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Cite this: *Dalton Trans.*, 2025, **54**, 16550

Dirhenium core-based cyclic and acyclic helicates as anticancer agents for breast cancer and skin cancer cells

Moon Kedia, [a] Sajmina Khatun,[b] Ramar Arumugam, [c] Chandra Lekha Putta,†[b] Bhaskaran Shankar,†[d] Upasana Phukon, [a] Vadapalli Chandrasekhar, [*c] Aravind Kumar Rengan [*b] and Malaichamy Sathiyendiran [*a]

The design and synthesis of dirhenium(I)-based heteroleptic helicates, *fac*-[Re(CO)$_3$(μ-L^n)(μ-**L^5**)Re(CO)$_3$] (**1–2**), where (L^n; *n* = 1, 3) **L^1** = 2,2′-(1,1′-((methylazanediyl)bis(4,1-phenylene))bis(benzoimidazole-2,1-diyl))diphenol, **L^3** = 2,2′-(1,1′-(oxybis(4,1-phenylene))bis(benzoimidazole-2,1-diyl))diphenol and **L^5** = bis(3-((1*H*-naphtho[2,3]imidazol-1-yl)methyl)-2,4,6-trimethylphenyl)methane, are reported along with two dinuclear acyclic helicates, *fac*-[Re(CO)$_3$(μ-L^n)$_2$Re(CO)$_3$] (**3–4**), where (L^n; *n* = 2, 4) **L^2** = 2-(1-(4-((4-bromophenyl)(methyl)amino)phenyl)-benzoimidazolyl)phenol and **L^4** = 2-(1-(4-(4-bromophenoxy)phenyl)-benzoimidazolyl)phenol. Solid state structures were confirmed by single crystal X-ray diffraction analysis, while ^{1}H-NMR data of **1–4** revealed the retention of the structures in the solution state as well. Cytotoxicity of these complexes was evaluated in triple-negative breast cancer cells (4T1) and skin cancer cells (B16). **1–4** showed greater cytotoxicity than the widely used medication cisplatin, and one of the helicates, **2**, was investigated further to assess the complex's antimetastatic properties and capacity to induce apoptosis by disrupting the membrane potential. Complex **2** was found to be lipophilic and displayed substantial stability in biological media.

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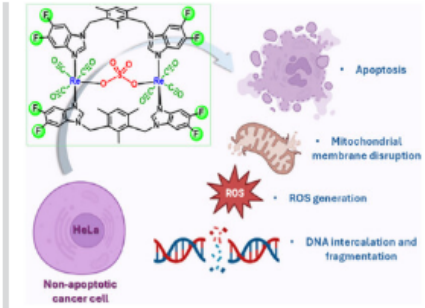
5 Chemistry - An Asian Journal, 2025, 20(11), e202401656

Full Access

Fluorine-Substituted Rhenium(I) Metallocycle: A New Class of Potent Anticancer Agent

Reema L. Borkar, Chandra Lekha Putta, Dr. Bhaskaran Shankar, Dr. Basu Bhattacharjee, Dr. Aravind Kumar Rengan, Dr. Malaichamy Sathiyendiran

e202401656 | First Published: 14 April 2025



Fluorinated compounds continue to receive considerable attention in medicinal chemistry owing to their remarkable enhancement in biological properties achieved through fluorine incorporation. Herein, the synthesis and biological evaluation of fluorinated and nonfluorinated dinuclear Re(I) tricarbonyl metallocycles are presented. The fluorinated metallocycle displayed significant anticancer activity against human cervical cancer cells compared to its nonfluorinated analogue, exhibiting greater efficacy than the clinically used cisplatin.

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Journal of Organometallic Chemistry 1015 (2024) 123238

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

fac-[M(CO)$_3$] (M = Mn or Re)-based capped metallacalix[3]arenes

Shruthi Bayya [a], Reema L. Borkar [a], Isha Mishra [a], Bhaskaran Shankar [b], Maruthupandiyan Priyatharsini [a], Malaichamy Sathiyendiran [a,*]

[a] School of Chemistry, University of Hyderabad, Hyderabad, 500046, India
[b] Department of Chemistry, Thiagarajar College of Engineering, Madurai, 625015, India

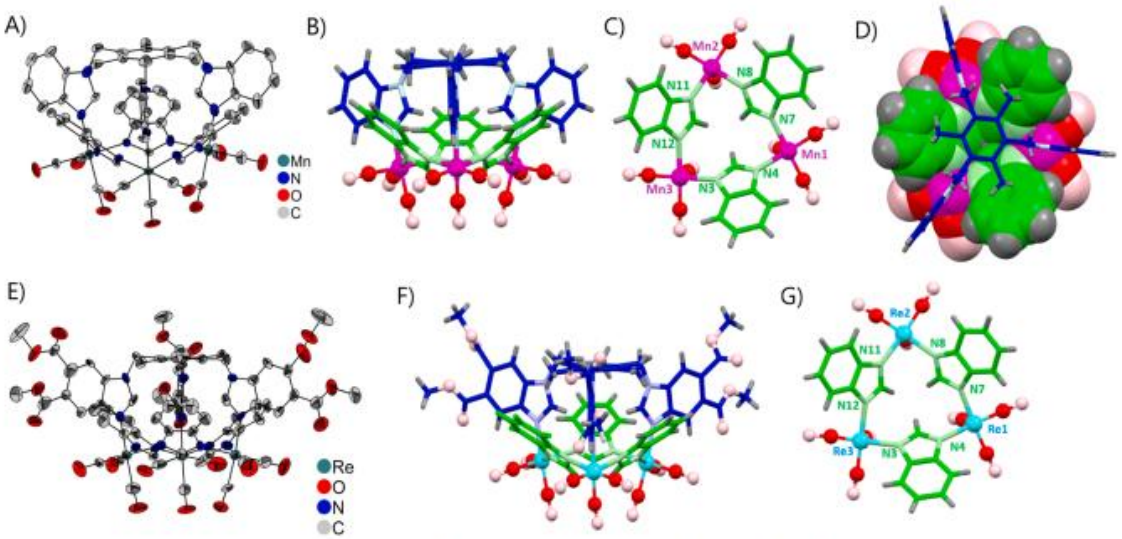


Fig. 4. Different views of molecular structures of capped metallacalix[3]arenes **1** (A, B, D) and **3b** (E and F). Thermal ellipsoid plot with 40 % probability of **1** (A) and **3b** (E), hydrogen atoms are omitted for clarity. Metallacalix[3]arene framework of **1** (C) and **3b** (G). Color code: Neutral N donor = blue, anionic N donor = green, H = grey, C of C≡O = red, O = pink, Re = cyan, Mn = magenta.

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Journal of Organometallic Chemistry 1014 (2024) 123199

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Flexible rhenium metallocages: Self-assembly, solid-state structures, and solution dynamics

Isha Mishra [a], Reema L. Borkar [a], Bhaskaran Shankar [b], Malaichamy Sathiyendiran [a,*]

[a] School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
[b] Department of Chemistry, Thiagarajar College of Engineering, Madurai 625015, India

ARTICLE INFO

Keywords:
Metallocages
Self-assembly
Rhenium
Butterfly
Solvothermal

ABSTRACT

Neutral heteroleptic tetranuclear rhenium coordination cages *fac*-[{Re(CO)$_3$(im)}$_4$(L)$_2$] (**1**) and *fac*-[{Re(CO)$_3$(tz)}$_4$(L)$_2$] (**2**) were self-assembled using $Re_2(CO)_{10}$, from carbonyldiimidazole (CO-im$_2$)/ 1,2,4-triazole (H-tz), and bis(benzimidazol-1-yl)methane (L) *via* a one-pot solvothermal approach. The cages were characterized using AT-IR, NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction analysis. The molecular structures of the cages indicate that the cage is composed of a tetranuclear cyclic core [(Re-im)]$_4$ or [(Re-tz)]$_4$ which resembles a butterfly, along with two dbim (L) ligand motifs positioned both above and below the tetranuclear motif. The cage **1** in DMSO exhibits flexibility, and its dynamic behavior was investigated through variable temperature ^{1}H NMR studies.

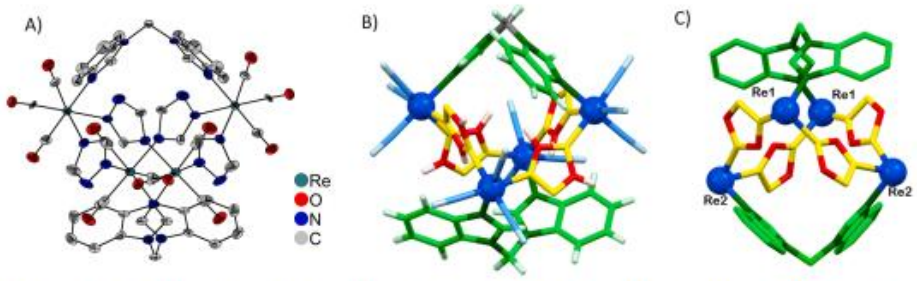


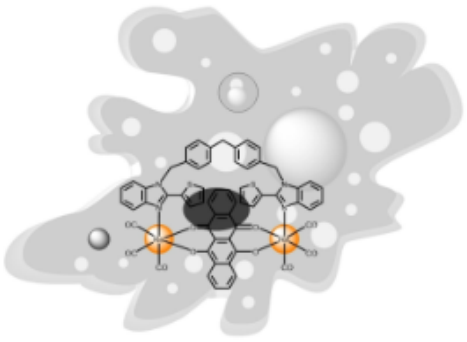
Fig. 2. Various views of molecular structure of **2** (A-C). Thermal ellipsoids plot of **2** is shown at a probability level of 50 % (A). H atoms are removed for clarity in A and C. CO groups are removed for clarity in C. Color code: blue = *fac*-[Re(CO)$_3$], red and yellow = C and N of 1,2,4-triazolate and green.

8 Chemistry - A European Journal, 2024, 30(32), e202400217.

Dinuclear Rhenium(I) Tricarbonyl Complexes as Anticancer Drug Candidates

Nicolás Montesdeoca, Reema L. Borkar, Malaichamy Sathiyendiran, Johannes Karges

e202400217 | First Published: 04 April 2024



In this study the chemical synthesis and biological evaluation of dinuclear rhenium(I) complexes as potential chemotherapeutic drug candidates are presented. The metal complexes primarily accumulated in the mitochondria, causing cell death by apoptosis. The lead compound demonstrated to eradicate a pancreatic carcinoma multicellular tumor spheroid upon treatment with micromolar concentrations.

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Solvent-Directed Rhenium(I) Metallocyclic Tubes, Dimeric Capsule, and Intercalated Dimers

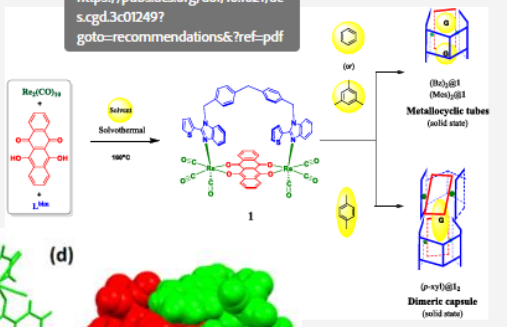
Reema L. Borkar, Mamina Bhol, Bhaskaran Shankar, Johannes Karges,* and Malaichamy Sathiyendiran*

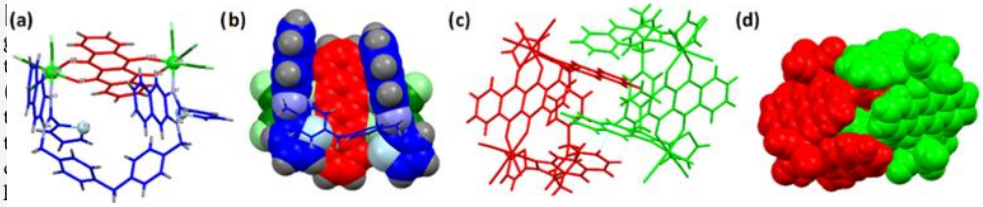
Cite This: *Cryst. Growth Des.* 2024, 24, 1987−1999 Read Online

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ABSTRACT: Neutral flexible bidentate nitrogen donor ligands L^n (L^{bim} and L^{nim}) were designed, synthesized, and utilized as structural frameworks to construct solvent-directed rhenium(I) metallocyclic tubes, dimeric capsules, and intercalated dimers in the solid state. The combination of $Re_2(CO)_{10}$, 6,11-dihydroxy-5,12-naphthacenedione (H_2-dhnq) or 1,4-dihydroxyanthraquinone (H_2-dhaq), and L^{bim} or L^{nim} in the presence of benzene (Bz), mesitylene (Mes), or *p*-xylene (*p*-xyl) resulted in neutral heteroleptic metallocyclic tubes *fac*-[{(CO)$_3$Re(μ−dhnq)Re(CO)$_3$}(μ−L^{bim})] (**1**), *fac*-[{(CO)$_3$Re(μ−dhnq)Re(CO)$_3$}(μ−L^{nim})] (**2**), or *fac*-

https://pubs.acs.org/doi/10.1021/acs.cgd.3c01249?goto=recommendations&?ref=pdf





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Journal of Organometallic Chemistry 1007 (2024) 123025

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Self-assembly of tetrarhenium Z-shaped metallosupramolecule

Reema L. Borkar, Malaichamy Sathiyendiran *

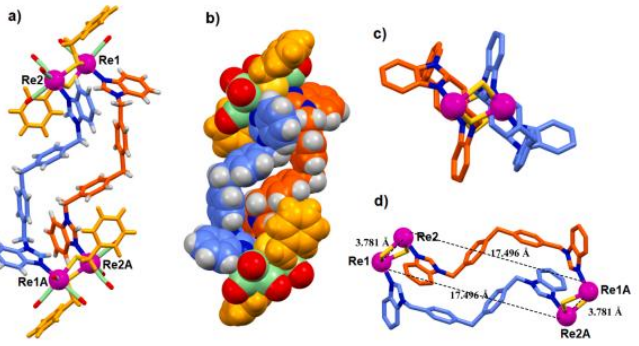
School of Chemistry, University of Hyderabad, Hyderabad, 500 046, India

ARTICLE INFO

Keywords:
Benzimidazolyl
Self-assembly
Metallosupramolecule
Rhenium
Supramolecule

ABSTRACT

Tetranuclear Z-shaped metallosupramolecule *fac*-[{(CO)$_3$Re(μ-SCH$_2$Ph)$_2$Re(CO)$_3$}$_2$(L)$_2$] (**1**) was self-assembled from the combination of $Re_2(CO)_{10}$, Ph-CH$_2$-S-S-CH$_2$-Ph, and flexible neutral bidentate N-donor ligand (L) *via* one-pot solvothermal approach. The complex was characterized by ^{1}H NMR, IR, ESI-mass analysis, and single crystal X-ray diffraction analysis. The solid state structure reveals that the metallosupramolecule consists of two flexible ligands (L) which are bridged by two [(CO)$_3$Re(μ-SCH$_2$Ph)$_2$Re(CO)$_3$] motifs resulting in a Z-shaped architecture.



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Journal of Organometallic Chemistry, 2024, 1004, 122937

Phosphine oxide donor-based dinuclear rhenium(I) metallocycles

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[b] Department of Chemistry, Chaudhary Bansi Lal University, Prem Nagar Campus, Bhiwani, Haryana 127 021, India
[c] Department of Chemistry, Thiagarajar College of Engineering, Madurai 625 015, India

ARTICLE INFO

Keywords:
Chloranilic acid
Metallocycle
Phosphine oxide
Rhenium
Supramolecule

ABSTRACT

Neutral binuclear metallocycles *fac*- [{Re(CO)$_3$}$_2$(CA)(L)] (**1**–**2**) were obtained using $Re_2(CO)_{10}$, flexible ditopic phosphine oxide donor 9,10-bis(dimethylphosphonomethyl)anthracene/ 9,10-bis(diethylphosphonomethyl) anthracene (L), and chloranilic acid (H_2–CA) in mesitylene *via* one-pot solvothermal methods. The metallocycles were characterized by E.A., FT-IR, ESI-MS and NMR analysis. The solid-state structures of **1**–**2** were confirmed by X-ray analysis which reveal that the complexes adopt binuclear heteroleptic cyclic architectures. The *fac*- [Re(CO)$_3$] core-based metallocycles **1**–**2** are two of the very few examples of phosphine oxide donor (P=O)-based supramolecular coordination cyclic complexes.

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CRYSTAL GROWTH & DESIGN

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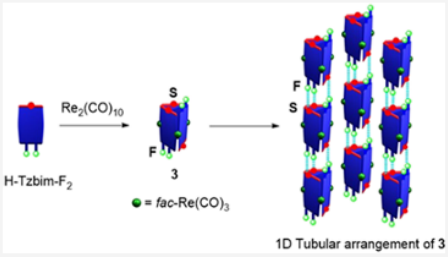
Fluorine-Assisted Self-Assembly Approach for Tubular Architecture of Cyclic Trinuclear Rhenium(I)-Fluorothiabendazolate Complex

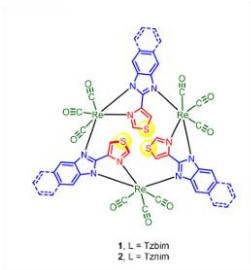
Isha Mishra, Bhaskaran Shankar, and Malaichamy Sathiyendiran*

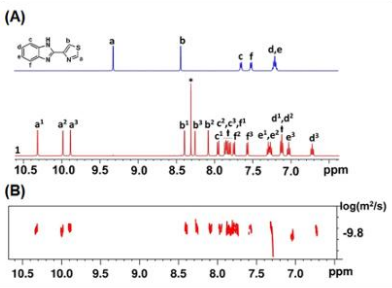
Cite This: *Cryst. Growth Des.* 2023, 23, 9103–9110 Read Online

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ABSTRACT: Three neutral trinuclear rhenium(I)-organic complexes, *fac*-[{Re(CO)$_3$(L)}$_3$] (**1**–**3**), were self-assembled using $Re_2(CO)_{10}$ and thiabendazole/thiazolyl naphthanoimidazole/difluorothiabendazole (H-L) via a one-pot approach. The molecular structures established by X-ray analysis revealed that **1**–**3** adopt an M_3L_3-type triangular structure which consists of alternatively arranged three *fac*-[Re(CO)$_3$] cores and three anionic ligand motifs. All three complexes possess uncoordinated sulfur atoms from the thiazolyl motif directed along the complex axis. Complex **3** additionally possesses six C–F bonds, four at one end and two at the rear, lateral to the complex axis which further self-organizes into 1D supramolecular tubular







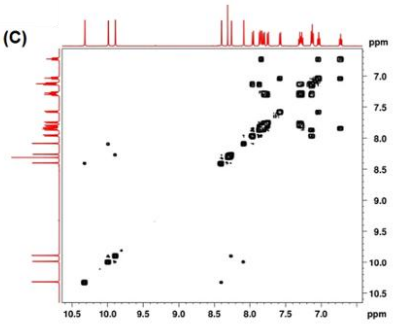


Figure 1. (A) Partial ^{1}H NMR spectra of H-Tzbim (blue) and complex **1** (red); and (B, C) DOSY and ^{1}H–^{1}H COSY spectra of **1** in d_6-DMSO (*chloroform solvent peak).

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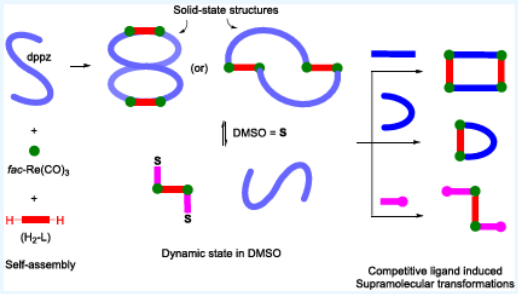
Rhenium–Pyrazolyl-Based Figure-Eight- and Z-Shaped Metallocycles: Self-Assembly, Solid-State Structures, Dynamic Properties in Solution, and Competitive Ligand-Induced Supramolecular Transformations into Rhenium-Pyridyl/-Benzimidazolyl/-Phosphine-Based Metallocycles/Acyclic Complexes

Upasana Phukon, Moon Kedia, Bhaskaran Shankar, and Malaichamy Sathiyendiran*

Cite This: *ACS Omega* 2023, 8, 41773–41784 Read Online

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ABSTRACT: Rhenium(I)tricarbonyl core-based heteroleptic "figure-eight"- and Z-shaped metallocycles (**1a**–**4a**) of the general formula *fac*-[{(CO)$_3$Re(μ-L)Re(CO)$_3$}$_2$(dppz)$_2$] were self-assembled from Re$_2$(CO)$_{10}$, H$_2$-L (H$_2$-L = 5,8-dihydroxy-1,4-naphthaquinone (H$_2$-dhnq) for **1a**; 1,4-dihydroxy-9,10-anthraquinone (H$_2$-dhaq) for **2a**; 6,11-dihydroxy-5,12-naphthacenedione (H$_2$-dhnd) for **3a**; 2,2′-bisbenzimidazole (H$_2$-bbim) for **4a**), and bis(4-((pyrazolyl)methyl)phenylmethane) (dppz) via one-pot coordination-driven synthetic approach. The molecular structures of **1a** and **4a** were unambiguously confirmed by single-crystal X-ray diffraction (SC-XRD) methods. The metallocycles in the DMSO solution exist as an acyclic dinuclear–DMSO adduct of the general formula *fac*-[{(CO)$_3$Re(μ-L)Re(CO)$_3$}(DMSO)$_3$] (**1b**, L = dhnq;



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Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

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DOI: 10.1039/d3dt02535g

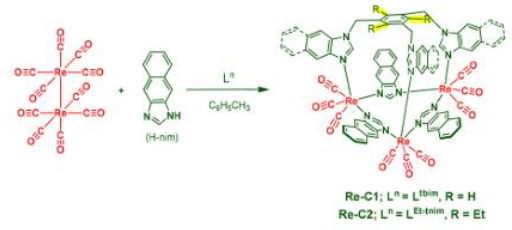
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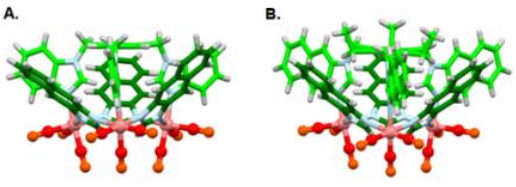
Trinuclear rhenium(I)-based metallocages as anticancer agents towards human cervical cancer cells†

Moon Kedia,[a] Sajmina Khatun,[b] Upasana Phukon,[a] Bhaskaran Shankar,[c] Aravind Kumar Rengan *[b] and Malaichamy Sathiyendiran *[a]

The first examples of spherical-shaped trinuclear rhenium(I) organometallic cages displaying cytotoxic, antimetastatic, antiproliferative and DNA-damaging behavior towards a human cervical (HeLa) cancer cell line are reported. The compact design of the metallocages facilitates their interactions with biosystems leading to comparable efficiency to that of the commonly used anticancer drug cisplatin.

Cancer is one of the deadliest invasive diseases with a high mortality rate worldwide. Although several conventional cancer therapies such as surgery, chemotherapy, and radiation therapy are available, most of the treatments cause severe side effects in cancer patients. Drug resistance is another factor that leads to the therapeutic limitations of conventional Pt-based drugs in cancer treatment. The toxic side effects of these Pt-based drugs such as cisplatin are a consequence of the covalent adducts formed between the complexes and DNA





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Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/jorganchem

Note

Rhenium(I)tricarbonyl M_2Cl_2L-type metallocycles from flexible ditopic benzimidazolyl donors

K.R. Soumya, Moon Kedia, Malaichamy Sathiyendiran*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

ARTICLE INFO

Article history:
Received 28 March 2023
Revised 25 April 2023
Accepted 27 April 2023
Available online 2 May 2023

Keywords:
Halide
Metallocycle
Naphthanoimidazole

ABSTRACT

Neutral binuclear metallocycles of the formula, *fac*-[{$(CO)_3Re(\mu\text{-}Cl)_2Re(CO)_3$}$L^n$] were obtained using $[Re(CO)_5Cl]$ and ditopic flexible nitrogen donor (L^n = L^1 = bis((benzimidazol-1-yl)methyl)benzene; L^2 = bis((5,6-dimethylbenzimidazol-1-yl)methyl)benzene, L^3 = bis((naphthanoimidazol-1-yl)methyl) benzene) in toluene under solvothermal approach. The metallocycles were characterized by ATR-IR, ^1H NMR and ESI- Mass analysis. The crystal structures of **1–3** were confirmed by single crystal X-ray diffraction analysis. Non-traditional intermolecular hydrogen bonding interactions (C-H···O=C) stabilize the solid state structures of the metallocycles.

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Inorganic Chemistry

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Self-Assembly of Rhenium(I) Double-Stranded Helicate and Mesocate from Flexible Ditopic Benzimidazolyl/ Naphthanoimidazolyl N-Donor and Rigid Bis-Chelating Hydroxyphenylbenzimidazolyl N∩OH-Donor Ligands: Synthesis, Characterization, and Photophysical and B-DNA Docking Studies

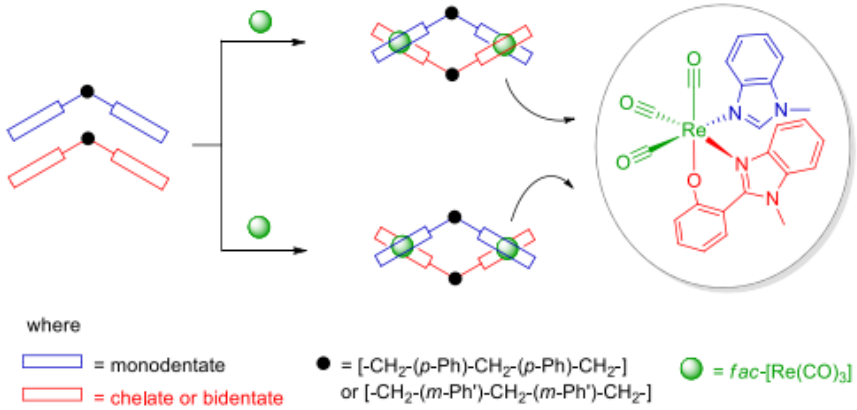
Mamina Bhol, Reema L. Borkar, Bhaskaran Shankar, Saroj Kumar Panda, Mariusz Wolff,* and Malaichamy Sathiyendiran*

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Scheme 1. Cartoon Representation of the Self-Assembly of *fac*-$Re(CO)_3$-Based Neutral Unsaturated Heteroleptic Dinuclear Double-Stranded Helicate and Mesocate



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CrystEngComm

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A double ouroboros-shaped noncovalent molecular dimer†

Moon Kedia, K. R. Soumya, Upasana Phukon, Isha Mishra, Reema L. Borkar, Palanichamy Vengadeshwaran, Mamina Bhol and Malaichamy Sathiyendiran *



Fig. 1 Mythological symbol of ouroboros as depicted by Lucas Jennis, in the 1625 alchemical tract De Lapide Philosophico (left) and double ouroboros with two different serpents (right).[2,6]

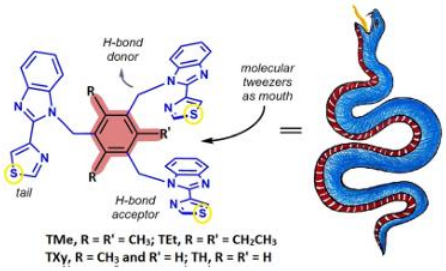


Fig. 2 Chemical structures of flexible tripodal molecules (**TMe**, **TEt**, **TXy**, and **TH**). One of the possible conformations shows a molecular tweezers-like opening at one end (left) and a cartoon representation of a snake (right).

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Aggregation-induced emission enhancement (AIEE) of tetrarhenium(I) metallacycles and their application as luminescent sensors for nitroaromatics and antibiotics†

Mohammad Nurnabi,[a] Shunmugasundaram Gurusamy,[b] Jing-Yun Wu,[c] Chung-Chou Lee,[a] Malaichamy Sathiyendiran,[a] Sheng-Ming Huang,[a] Che-Hao Chang,[a] Ito Chao,[a] Gene-Hsiang Lee,[d] Shie-Ming Peng,[d] Veerasamy Sathish,[e] Pounraj Thanasekaran *[f] and Kuang-Lieh Lu*[a,g]

The self-assembly of tetrarhenium metallacycles $[\{Re(CO)_3\}_2(\mu\text{-dhaq})(\mu\text{-N–N})]_2$ (**3a**, N–N = 1,3-bis(1-butylbenzimidazol-2-yl)benzene; **3b**, N–N = 1,3-bis(1-octylbenzimidazol-2-yl)benzene), (H_2-dhaq = 1,4-dihydroxy-9,10-anthraquinone) and $[\{Re(CO)_3\}_2(\mu\text{-thaq})(\mu\text{-N–N})]_2$ (**4**, N–N = 1,3-bis(1-butylbenzimidazol-2-yl)benzene), (H_2-thaq = 1,2,4-trihydroxy-9,10-anthraquinone) under solvothermal conditions is described. The metallacycles **3a,b** and **4** underwent aggregation-induced emission enhancement (AIEE) in THF upon the incremental addition of water. TEM images revealed that metallacycle **3a** in a 60% aqueous THF solution formed rectangular aggregates with a wide size distribution, while a 90% aqueous THF solution resulted in the formation of a mixture of nanorods and amorphous aggregates due to rapid and abrupt aggregation. UV-vis and emission spectral profiles supported the formation of nanoaggregates of metallacycles **3a,b** and **4** upon the gradual addition of water to a THF solution containing metallacycles. Further studies indicated that these nanoaggregates were excellent probes for the sensitive and selective detection of nitro group containing picric acid (PA) derivatives as well as antibiotics.

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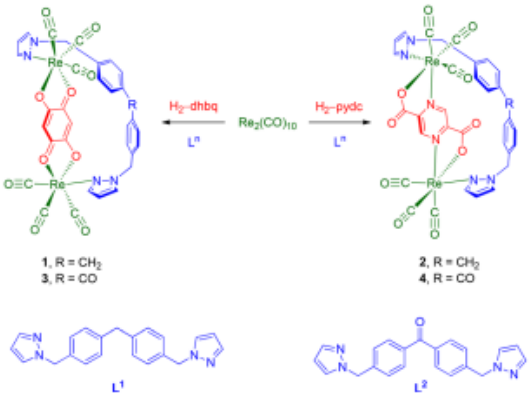
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Self-assembly of a new class of rhenium(I)-based double stranded dinuclear monohelicates with their photophysical and electrochemical studies†

Upasana Phukon,[a] Bhaskaran Shankar[b] and Malaichamy Sathiyendiran*[a]



Scheme 1 Self-assembly of helicates **1–4**.

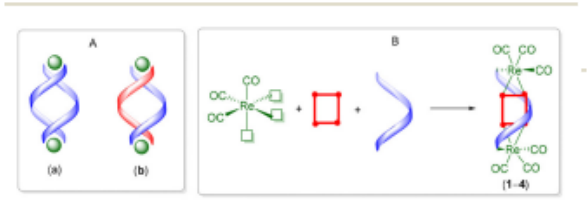


Fig. 1 (A) Commonly observed double-stranded dinuclear (a) homoleptic and (b) heteroleptic double helicates. (B) The design principle of new forms of double-stranded dinuclear monohelicates **1–4**.

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Rhenium(I)-Based Neutral Coordination Cages with a Spherical Cavity for Selective Recognition of Fluoride

Moon Kedia, Bhaskaran Shankar, and Malaichamy Sathiyendiran*

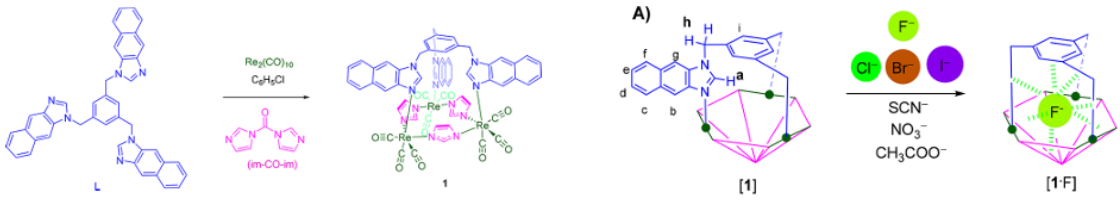
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ABSTRACT: Neutral heteroleptic trinuclear coordination cages containing a preorganized well-defined small spherical endocavity, which is made up of electron-deficient bowl frameworks, three coordination-induced neutral polar C−H donors, and a phenyl motif, were self-assembled via a one-pot approach; the endocavity accommodates fluoride selectively in the presence of other halides.

Scheme 1. Synthesis of the Neutral Coordination Cage 1



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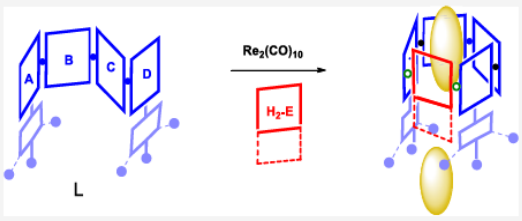
Rhenium(I)-Based Heteroleptic Pentagonal Toroid-Shaped Metallocavitands: Self-Assembly and Molecular Recognition Studies

Mamina Bhol, Bhaskaran Shankar, and Malaichamy Sathiyendiran*

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ABSTRACT: A family of neutral, heteroleptic, dinuclear M_2LL'-type pentagonal toroid-shaped metallomacrocycles (**1**−**8**) were synthesized using flexible ditopic N donors ($L^n = L^1-L^2$), rigid bis-chelating ligands ($H_2-L' = H_2-E$), and $Re_2(CO)_{10}$ in a one-pot solvothermal self-assembly approach. The ligands and the metallomacrocycles were characterized using ATR-IR, electrospray ionization mass spectrometry, nuclear magnetic resonance, ultraviolet−visible, and emission spectroscopy methods. The molecular structures of **1**, **2**, **4**, **6**, and **7** were confirmed by an X-ray diffraction



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Calix[4]arene-Analogous Technetium Supramolecules

Mamina Bhol, Guilhem Claude, Maximilian Roca Jungfer, Ulrich Abram,* and Malaichamy Sathiyendiran*

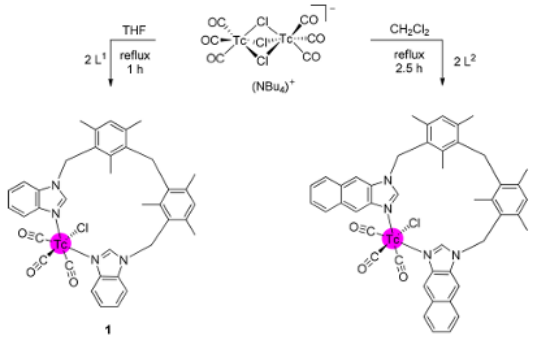
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ABSTRACT: Calix[4]arene-analogous technetium supramolecules (**1** and **2**) were assembled using $(NBu_4)[Tc_2(\mu\text{-}Cl)_3(CO)_6]$ and neutral flexible bidentate nitrogen-donor ligands (L^1 and L^2) consisting of four arene units covalently joined via methylene units. The neutral homoleptic technetium macrocycles adopt a partial cone/cone-shaped conformation in the solid state. These supramolecules are the first example of *fac*-$[Tc(CO)_3]^+$ core-based metallocalix[4]arenes and second example of *fac*-$[Tc(CO)_3]^+$ core-based metallomacrocycles. Structurally similar *fac*-$[Re(CO)_3]^+$ core-based macrocycles (**3** and **4**) were also prepared using $[Re(CO)_5X]$ (where X = Cl or Br) and L^1 or L^2. The products were characterized spectroscopically and by X-ray analysis.

The design and synthesis of stable and kinetically inert *fac*-$[M(CO)_3]^+$ (M = ^{99m}Tc/$^{186/188}$Re) core-based complexes have been gaining continuous research interest for the development of new radiopharmaceuticals as diagnostic and therapeutic agents.[1−17] ^{99m}Tc is still the workhorse of nuclear diagnostics because of its ideal nuclear decay properties ($t_{1/2}$ = 6.02 h, pure γ emitter, and E_γ = 140 keV, 89%), whereas the β-emitting rhenium nuclides ^{188}Re ($t_{1/2}$ = 17 h and E_β = 2.12 MeV) and ^{186}Re ($t_{1/2}$ = 89.3 h and E_β = 1.07 MeV) have potential for therapy.[2] Isostructural technetium and rhenium complexes are good candidates for nuclear medical theranostics, and procedures exist for the synthesis of aqua complexes $[^{99m}Tc/^{188}Re(CO)_3(H_2O)_3]^+$ as appropriate precursor molecules.[1c,2b,4,6] Several attempts have been made toward the synthesis of organometallic technetium complexes using various types of heterocyclic ligands because of their importance in medicinal fields.[1−17] Recently, efforts have been directed toward the design and synthesis of *fac*-flexible bidentate nitrogen donors (L^1 for **1** and L^2 for **2**; Scheme 1).

Scheme 1. Synthesis of Technetium Metallocalix[4]arenes



23 Prototype rhenium metallocavitand with four exocyclic cavities for small molecules
Kedia, Moon,Priyatharsini, Maruthupandiyan,Deval Sathiyashivan, Shankar,... Krishnakumar, Rajaputi Venkatraman,**Sathiyendiran, Malaichamy**
Journal of Organometallic Chemistry, 2022, 959, 122123

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Soumya, K. R.,Mishra, Isha,Kedia, Moon,... Borkar, Reema L.,**Sathiyendiran, Malaichamy**
Supramolecular Coordination Complexes: Design, Synthesis, and Applications, 2022, pp. 133–158

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