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Self-Assembly of Oxamidato Bridged Ester Functionalised Dirhenium Metallastirrups: Synthesis, Characterisation and Cytotoxicity Studies

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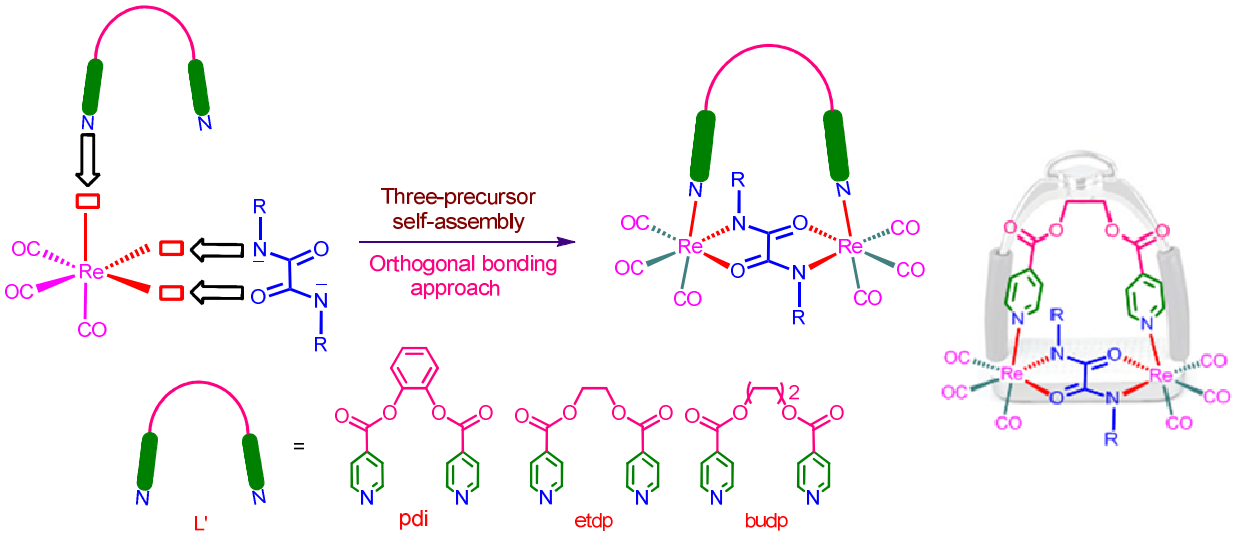


Hetero-topic self-assembly of $Re_2(CO)_{10}$ with oxamide ligands and ester-functionalised flexible ditopic-tectons afforded dinuclear metallacycles resembling a stirrup. The metallastirrups showed promising cytotoxic activity against few cancer cell lines *in-vitro*.

ABSTRACT: A new set of ester functionalised Re(I)-based oxamidato bridged neutral dinuclear metallacycles were synthesised by self-assembly of four components from three building blocks in a facile one-pot reaction via orthogonal bonding approach. Oxidative addition of oxamide ligands (H_2L = N,N′-diphenyloxamide, and N,N′-dibenzyloxamide) to rhenium carbonyl ($Re_2(CO)_{10}$) in the presence of semi-rigid and flexible ditopic pyridyl ligands (L′ = *o*-phenylene diisonicotinate (pdi), ethane diyl di-4-pyridine carboxylate (etdp) and 1,4-butane diyl di-4-pyridine carboxylate (budp)) having ester functionality afforded neutral dirhenium metallacycles of general formula $[(CO)_3Re(\mu\text{-}L)(\mu\text{-}L')Re(CO)_3]$ (**1**–**5**) under solvothermal reaction conditions. The metallacyclic compounds were characterised using elemental analyses, IR, UV−vis and NMR spectroscopic techniques. Structural analyses of **2**–**5** by single crystal X-ray diffraction methods revealed a stirrup like molecular framework in which two *fac*-$Re(CO)_3$ units are bridged together by dissymmetrical NO∩ON bis-chelation of oxamide ligands (as pedestal of stirrups) and further connected by a flexible ditopic tecton (as arched anchor of stirrups) in an orthogonal fashion. The cytotoxicity activities of dirhenium metallacycles **1**–**5** were studied *in vitro* against three different cancer cell lines and normal cells.

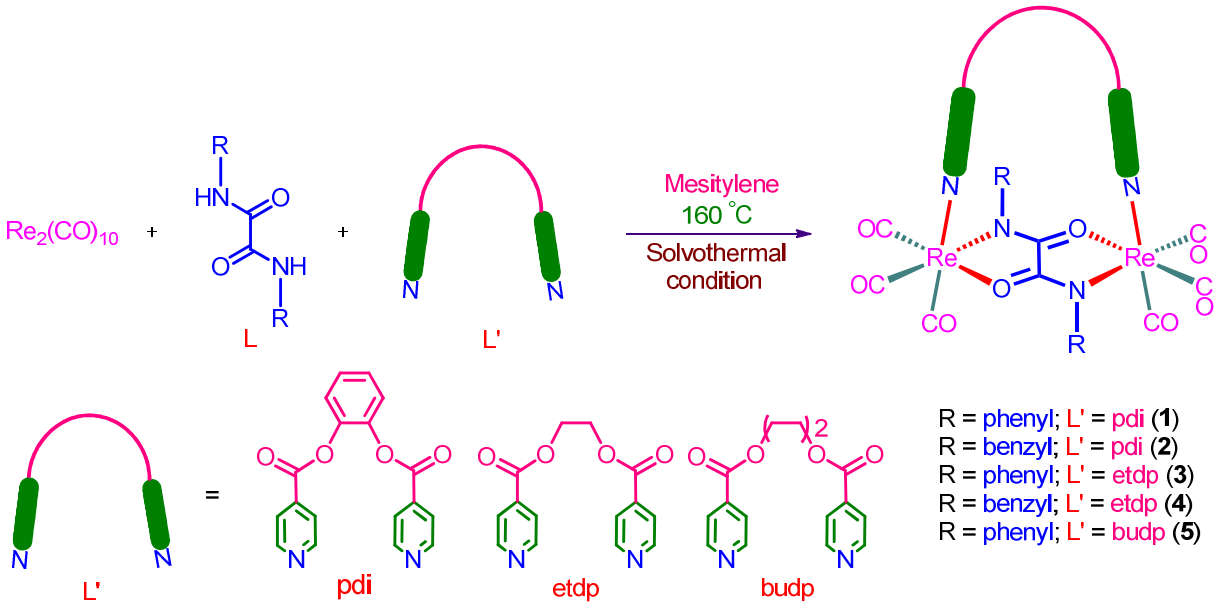
Keywords: Self-assembly; Orthogonal bonding; dinuclear metallastirrups; ester functionalisation; cytotoxicity studies.

Introduction

Exploiting metal directed self-assembly has garnered a thriving interest owing to its simplicity to fabricate a broad spectrum of two- and three-dimensional metal based frameworks under the giant umbrella of metallacyclophanes.[1–10] From the wide variety of diverse transition-metal based metallacyclophanes, *fac*-$Re(CO)_3$ based supramolecular architectures have been greatly exploited owing to their fascinating photophysical, sensing, and catalytic properties.[11–13] Besides their stability and having interesting excited state luminescent properties, rhenium based metallacyclophanes were probed for studying host-guest chemistry involving charge transfer via chromophore-quencher complex formation.[14,15] Some of the Re(I)-based compounds also showed promising anti-cancer activity.[16] A variety of Re(I)-based metallacyclophanes have been developed by exploiting orthogonal bonding approach via hetero-ligand self-assembly using various bis-chelating moieties.[17,18] Among the diverse shaped rhenium based molecular ensembles, *fac*-$Re(CO)_3$ core containing dirhenium metallacycles are relatively less explored.[13a,19] Lu and co-workers developed few NN∩NN and OO∩OO coordinated rhenium(I)-based dinuclear metallacyclic compounds containing flexible ditopic ligands in one-step fashion.[20] Incorporation of flexible ligands in the molecular frame work offers adaptive recognition and breathing ability in solid state.[21] Akin to molecular-sized metallacyclic rotors,[20a] a new family of molecular stirrups has been developed by the self-assembly of cis-protected palladium, ditopic rigid ligand and flexible pyridyl-pyrazolyl linkers.[22] Availability of various flexible ditopic ligands and wide range of bis-chelating moieties that serves as an anchor and base of the stirrup framework respectively, offer a broad scope to develop a variety of rhenium based dinuclear stirrup like metallacycles. Among various bis-chelating ligands, N,N′-di(alkyl/aryl)oxamides exhibit biological activity and DNA binding ability in addition to symmetrical or dissymmetrical bis-chelation with various metal ions.[23,24] Some oxamidato bridged arene ruthenium compounds have been developed out of which few dinuclear

complexes showed excellent selectivity for cancer cells.[25] However, oxamidato bridged neutral rhenium based metallacycles yet remained scarce and has a great scope for exploration.[26] Although very few reports pertaining to three precursor self-assembled dirhenium metallacycles having flexible linkers as aforementioned are available, incorporation of functionalised ditopic flexible ligands and their cytotoxicity evaluation remains to be eluted. In this scenario, synthesis of rhenium based metallacyclophanes using NO∩ON bis-chelating oxamidato moiety has got a great deal of attention. Hence, herein we report on the synthesis of oxamidato bridged rhenium based metallastirrups via three precursor hetero-topic self-assembly of rhenium carbonyl and dianionic bis-chelating oxamide ligands in presence of flexible ester functionalised ditopic tectons in a facile one-pot reaction under solvothermal conditions. The metallastirrup compounds were spectroscopically and structurally characterised. The ester functionalised ligands and dinuclear metallacyclophanes **1**–**5** were probed to study their anti-cancer activity using cisplatin as reference against three cancer cell lines and normal cells. The compounds selectively and differentially inhibited cancer cells while their ligand precursors were inactive.

Results and discussion



Scheme 1 One-step synthesis of rhenium based oxamidato bridged dinuclear metallastirrups, $[(CO)_3Re(\mu\text{-}L)(\mu\text{-}L')Re(CO)_3]$ (**1**–**5**).

Three-precursor self-assembly of rhenium carbonyl ($Re_2(CO)_{10}$), oxamide ligands (H_2L = N,N′-diphenyloxamide (dpo) and N,N′-dibenzyloxamide (dbno)) and ester functionalised flexible ditopic linker (L′ = *o*-phenylene diisonicotinate (pdi), ethane diyl di-4-pyridine carboxylate (etdp) and 1,4-butane diyl di-4-pyridine carboxylate (budp)) in an equimolar ratio led to the formation of novel rhenium based oxamidato bridged dinuclear stirrup like metallacycles of general formula $[(CO)_3Re(\mu\text{-}L)(\mu\text{-}L')Re(CO)_3]$ (**1**–**5**). The metallastirrups were synthesised under facile one-pot reaction using solvothermal conditions in mesitylene medium (Scheme 1). When rhenium carbonyl was treated with oxamide ligands in presence of flexible pyridyl linker, oxamide ligands were oxidatively added across Re–Re bond via dissymmetrical ON∩NO bis-chelation along with coordination of flexible ditopic ester functionalised pyridyl ligands in an orthogonal fashion to

afford dinuclear metallastirrups. Semi-rigid and flexible pyridyl ligands containing ester functionality have been incorporated in the skeletal framework of self-assembled dirhenium metallastirrups. Compounds **1**–**5** were stable towards air, light and moisture and were soluble in common organic solvents.

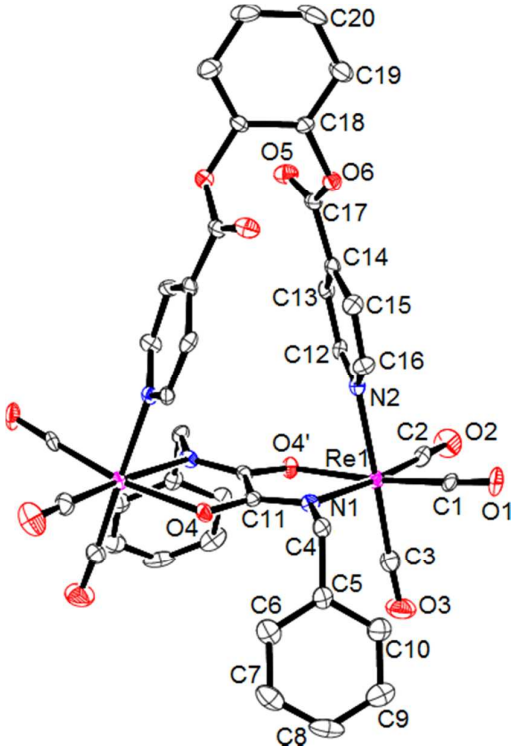


Fig. 1 ORTEP diagram of dibenzyloxamidato bridged dirhenium metallastirrup $[(CO)_3Re(\mu\text{-dbno})(\mu\text{-pdi})Re(CO)_3]$ (**2**) with thermal ellipsoids at 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for **2**

Re1–N1	2.181(7)	O4′–Re1–N1	76.0(3)
Re1–N2	2.210(7)	O4′–Re1–N2	80.1(3)
Re1–O4′	2.158(7)	N1–Re1–N2	84.7(3)
Re1–C1	1.906(9)	C1–Re1–N1	98.8(3)
Re1–C2	1.931(10)	C1–Re1–N2	92.2(3)
Re1–C3	1.940(10)	C3–Re1–N1	94.1(3)

Metallastirrups **1**–**5** were characterised using IR, UV-vis, and NMR spectroscopic techniques and elemental analyses. IR spectra of compounds **1**–**5** in CH_2Cl_2 displayed strong bands in the region of $\nu_{(CO)}$ 1895 to 2029 cm^{-1} with similar pattern characteristic to facial assembly of three terminal carbonyls (*fac*-$Re(CO)_3$) in an octahedrally coordinated metal centre.[26,27] The C=O stretching frequency of bis-chelated oxamidato moiety appeared as a strong band at around of 1595 to 1610 cm^{-1}, while that of free oxamide ligands (H_2L) appeared at 1650 cm^{-1}. The disappearance of NH stretching bands and the shifting of the C=O stretching frequency in metallastirrups **1**–**5** in comparison to the signals of free oxamide ligands (H_2L) indicated the chelation of oxamide ligands with rhenium centers. The ester C=O stretching frequency of flexible ditopic ligands in **1**–**5** appeared as a medium-intensity band in the range of 1735–1763 cm^{-1}. UV–visible spectra of compounds **1**–**5** showed similar absorption pattern that displayed three bands. Two absorption bands in higher energy region at around λ_{max} 227 and 267 nm were assigned to ligand-centered π–π* and n–π* transitions respectively. Another absorption band observed in lower energy region in the range of λ_{max} 324–340 nm was attributed to MLCT transition.[26,28] Emission spectra of compounds **1** and **2** showed broad emission at λ_{max} 436 and 429 nm while metallacycles **3** and **4** displayed emission at around 585 nm.[19b,26]

Formation of oxamidato bridged dirhenium metallastirrups **1**–**5** was further supported by ^1H and ^{13}C NMR spectral characterisation. ^1H NMR spectra of **1**–**5** showed two doublet of doublets, corresponding to H^2 and H^3 protons of pyridyl moiety in the range of δ 8.48–8.04 and 7.87–7.36 ppm respectively that were shifted downfield in comparison to those of free ligands. Aromatic protons of aryl substituted oxamidato bridge and anchor ligand (pdi) appeared as multiplets in the region of δ 7.57–7.06 ppm. Signals due to aliphatic protons amidst the ester functional groups in compounds **3**–**5** emerged as multiplets in the range of δ 5.20–2.10 ppm. Benzyl CH_2 protons of **2** and **4** appeared as two doublets in the region of δ 5.03–4.64 ppm that are attributed to two

diastereotopic protons.[26] ^{13}C NMR spectra of **1**–**5** displayed three signals of equal intensity for terminal carbonyls in the range of δ 197–194 ppm. Signal corresponding to amide carbonyl carbon appeared at around δ 171 ppm while ester carbonyl carbon emerged in the range of δ 163–161 ppm. In addition, the ^{13}C NMR spectra of **1**–**5** displayed appropriate signals relevant to various types of aromatic and aliphatic carbons present in the dinuclear architecture.

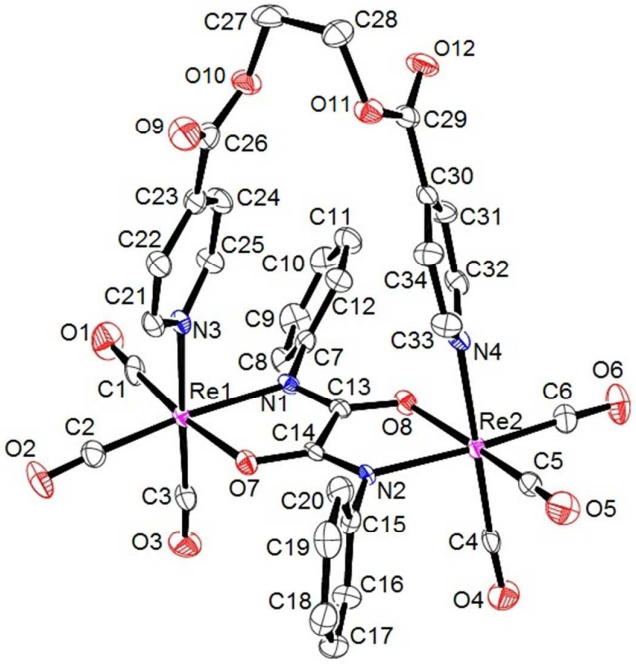


Fig. 2 ORTEP diagram of diphenyloxamidato bridged dirhenium metallastirrup [$(CO)_3$Re(μ-dpo)(μ-etdp)Re$(CO)_3$] (**3**) with thermal ellipsoids at the 50% probability level.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Re1–N1	2.197(4)	O7–Re1–N1	75.57(14)
Re1–N3	2.214(4)	N1–Re1–N3	84.38(14)
Re1–O7	2.153(4)	O7–Re1–N3	82.79(14)
Re1–C1	1.900(6)	C1–Re1–N1	99.50(19)
Re1–C2	1.912(5)	C1–Re1–N3	92.7(2)
Re1–C3	1.918(5)	C3–Re1–N1	94.74(18)

Good quality crystals of **2** and **5** suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of concentrated solutions of the compounds in dichloromethane, while single crystals of **3** and **4** were acquired from solvothermal reactions. The molecular structure and salient structural features of the compounds **2–5** accessed by single crystal X-ray diffraction studies, revealed dinuclear framework for the oxamidato bridged dinuclear compounds $[(CO)_3Re(\mu\text{-}L)(\mu\text{-}L')Re(CO)_3]$. Compounds **2** and **5** crystallised in space group *Pccn* and *P*21/*c* respectively, whereas compounds **3** and **4** crystallised in *P*21/*n* space group. The molecular structures of compounds **2–5** are given in Figures 1, 2, S1 and 3 respectively, and selected bond lengths and angles of the corresponding compounds are given in Tables 1, 2, S1 and 3 respectively. The crystallographic data and structural refinement details of **2**–**5** are given in Table S2.

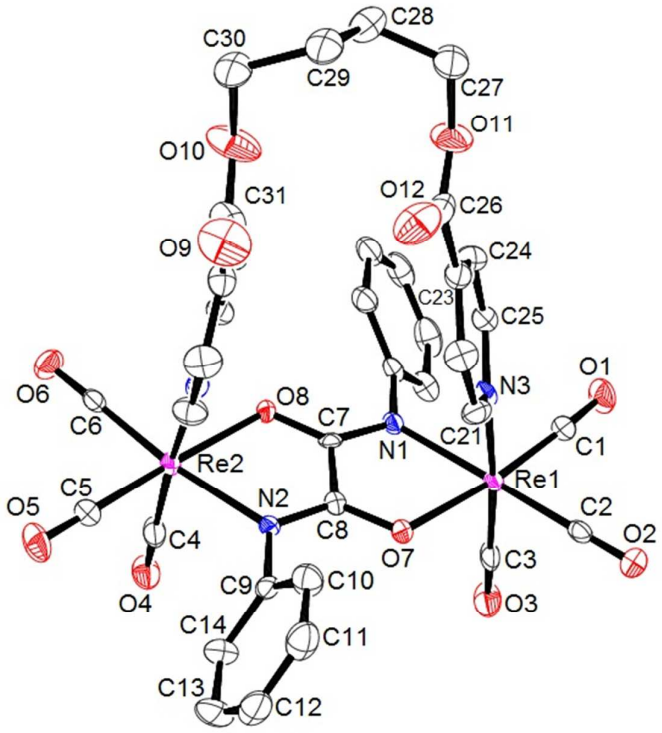


Fig. 3 ORTEP diagram of diphenyloxamidato bridged dirhenium metallastirrup $[(CO)_3Re(\mu\text{-dpo})(\mu\text{-budp})Re(CO)_3]$ (**5**) with thermal ellipsoids at the 50% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for **5**

Re1–N1	2.192(4)	O7–Re1–N1	75.85(15)
Re1–N3	2.206(4)	N1–Re1–N3	81.55(15)
Re1–O7	2.156(3)	O7–Re1–N3	81.84(14)
Re1–C1	1.916(6)	C1–Re1–N3	95.1(2)
Re1–C2	1.928(6)	C2–Re1–N3	93.28(19)
Re1–C3	1.912(6)	C3–Re1–N1	95.8(2)

ORTEP diagrams of **2**–**5** revealed a stirrup-like dinuclear skeletal framework with similar structural features, in which each rhenium centre is bonded to three carbonyls, one nitrogen and one oxygen atom of oxamidato bridge and another nitrogen atom from flexible pyridyl ligand in an octahedral fashion around it. The structural arrangement in **2**–**5** shows that two *fac*-$Re(CO)_3$ units are bridged by an oxamidato unit via dissymmetrical ON∩NO bis-chelation and furthermore the two rhenium centres are connected by a flexible ester functionalised ditopic pyridyl ligand. The oxamidato bridging unit and the dipyridyl ligands are orthogonally bonded to metal centres, leading to molecular stirrup like metallacyclic architecture. Two crystallographically independent molecules are present in the asymmetric unit of **3**. In metallastirrups **2**–**4**, the ester carbonyl groups are *anti* aligned whereas in **5**, they aligned *syn*. Structural insight of **2**–**4** shows that *syn* configuration of the ester carbonyl groups is not preferred probably due to steric hindrance caused by the rigidity of the phenyl/ethyl tethers, whereas in case of **5**, the syn configuration of carbonyl groups may be free with increasing flexibility. Phenyl rings of diphenyloxamidato bridge are tilted out of ON∩NO coordinating plane in case of **3** and **5**. As the flexibility of dipyridyl ligands increases, the centroid···centroid distance between the pyridyl rings also increases (**2** > **3** > **5**). Notably, Re···Re non-bonding distances (5.175–5.750 Å) were also increased in the same order (Figure 4). Atoms C28–C36 and O10–O12 of **4** and atoms C29 and C30 of **5** are positionally disordered with

occupancies of 56/43 and 71/29 respectively. Bond parameters around each rhenium centre are comparable with that of oxamidato bridged rhenium based molecular rectangles reported recently.[26] Apart from isoskeletal features, these dinuclear ensembles exhibit several of CH···O type non-covalent interactions in their solid state leading to interesting packing arrangements.

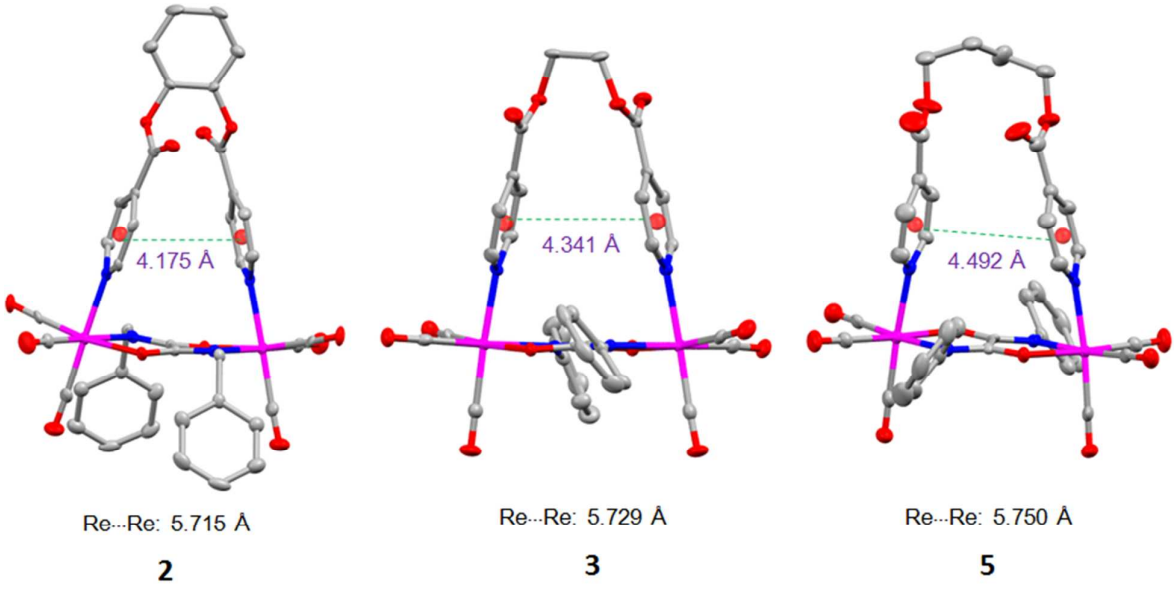


Fig. 4 Increase in Re···Re non-bonding distance with increase in the flexibility of the ester functionalised ditopic linker.

Compound **2** showed a CH···O type hydrogen bonding interactions originated from metal carbonyls, C(4)−H(4)···O(1) and C(12)−H(12)···O(1) with an interaction distance of 2.683 Å and 2.615 Å respectively.[29] Another type of CH···O interaction was observed from ester functionality, C(21)−H(21)···O(5) with a distance of 2.478 Å. A CH···π interaction was also observed from a central phenyl proton of 'pdi' ligand with aromatic moiety of the oxamide ligand (C(19)−H(19)···C(8)) with a distance of 2.751 Å.[30] A pyridyl and phenyl hydrogens (H(31) and H(11)) of compound **3** are involved in CH···O interaction with O(4) and O(13) of adjacent molecule with an interaction distance of 2.588 and 2.644 Å respectively. Another hydrogen bonding

interaction was observed from carbonyl oxygen (C(32)−H(32)···O(9)) with a distance of 2.270 Å. Benzyl hydrogen in compound **4** showed C(7)−H(7)···O(2) interaction with a metal carbonyl oxygen with an interaction distance of 2.713 Å, while another CH···O type interaction was observed from ester carbonyl oxygen O(9) with phenyl hydrogens H(20) and H(21) showing an interaction distance of 2.649 and 2.668 Å respectively (Figure 5). Compound **5** also displayed a CH···O type interaction that observed from pyridyl and phenyl hydrogens (H(36) and H(16)) with O(5) of metal carbonyl with an interaction distance of 2.589 and 2.709 Å respectively.

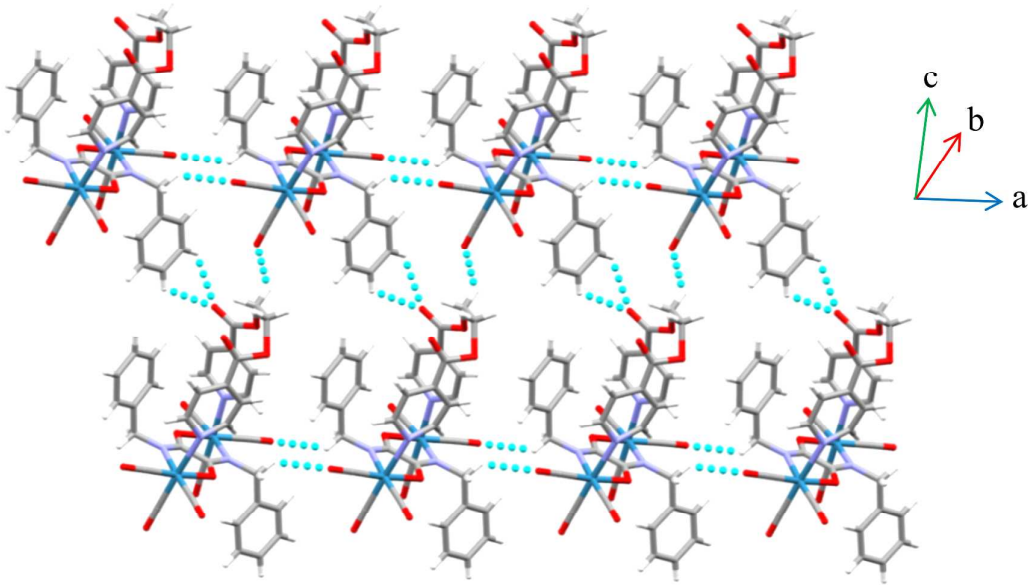


Fig. 5 Packing diagram of $[(CO)_3Re(\mu\text{-bbzo})(\mu\text{-etdp})Re(CO)_3]$ (**4**) showing various intermolecular CH···O hydrogen bonding interactions (blue dotted lines).

***In vitro* cytotoxicity studies**. The organic linkers employed in the construction of **1**–**5** were composed of varying length, flexibility and ester functionality in their framework which can play considerable role in tuning the cytotoxic activity.[31,32] In this study, the cytotoxic activities of compounds **1**–**5**, their ligands, $Re_2(CO)_{10}$ and cisplatin (positive control) were evaluated by MTT assay in three different cancer cell lines, namely lung (A549), cervical (HeLa) and colon (HCT-15),

and normal blood cells (PBMCs). The results showed that metallastirrup compounds **1**–**5** inhibited cancer cells exclusively in differential and dose-dependent manner (Figure S2-S7), while $Re_2(CO)_{10}$ and the ligands were found to be inactive in cancer and normal cells. As a representative of these compounds, **3** was dissolved in DMSO-d_6 and, using ^{1}H NMR spectroscopy, was found to be stable even after 48 h. Among the five compounds, compound **5** with longer alkyl chain exhibited anticancer activities with higher potency in two of the cancer cell lines (A549 and HCT-15) studied, although, compound **1** was most active (IC_{50} concentration of 20.8 ± 1.9 μM) particularly in colon (HCT-15) cancer cells while **3** was active in cervical (HeLa) cancer cells (Table. 4). The budp containing compound is more active than the etdp and pdi containing compounds and based on the cytotoxic studies (Mean IC_{50} concentrations and cancer cell lines), the comparative inhibitory potency of the compounds in decreasing activity are in order **5** > **4** > **2** > **3** > **1**. This observation is in accordance with the previously reported rhenium based compounds with flexible linkers.[16b,32] To study further whether the compounds induced cell death in cancer cells, morphological observations cancer cells treated with compounds **1** and **5** were performed. The IC_{50} concentration of compounds **1** and **5** treated cancer cells exhibited morphological features of apoptosis such as cell shrinkage, dead and floating cells in live cell imaging and nuclear condensation and formation of apoptotic bodies in fluorescent staining (Figure 6 and 7).

Table 4 IC_{50} values (μM) of compounds **1**–**5** after 48 h of exposure on lung (A549), cervical (Hela) and colon (HCT-15) cancer and normal (PBMCs) cell lines

Compound	Lung (A549)	Cervical (Hela)	Colon (HCT-15)	PBMCs
1	95.72±8.2	>100	20.80±1.9	na
2	56.15±2.9	54.19±2.4	na	na
3	88.49±1.2	29.81±2.5	na	na
4	65.23±7.2	40.49±1.9	na	na
5	29.65±1.4	64.50±1.9	30.53±1.3	na
Cisplatin	25.89±1.8	39.84±6.4	23.93±2.8	na

na = not active (less than 20% inhibition of cancer cells was observed at higher concentration (>100 μM) of compounds tested)

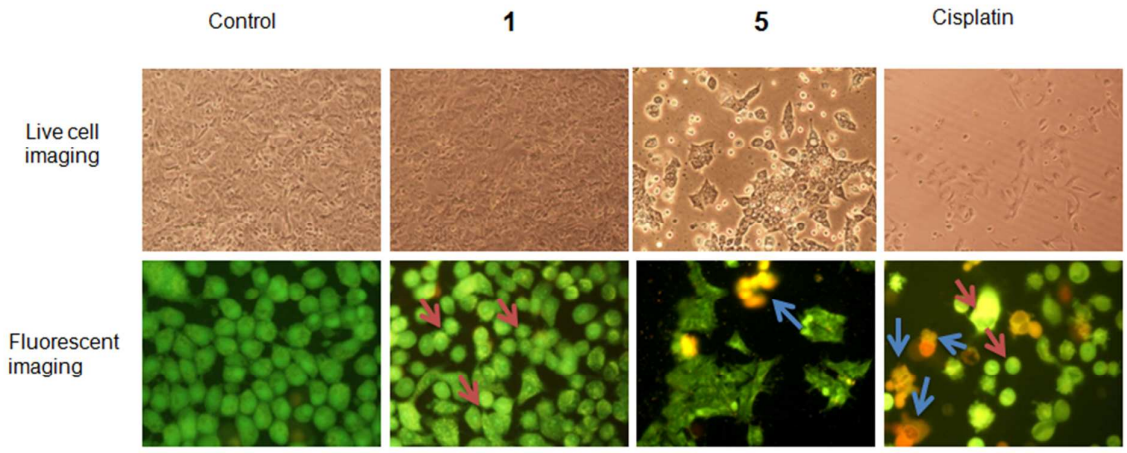


Fig. 6 Morphological observations of respective IC_{50} concentration of compounds **1**, **5** and cisplatin treated colon (HCT-15) cancer cells showing cell shrinkage, dead and floating cells by live cell imaging and early (red arrow indicating nuclear condensed bright yellowish green cells) and late (blue arrow indicating the DNA fragmentation and formation apoptotic bodies) apoptotic cells by fluorescent imaging.

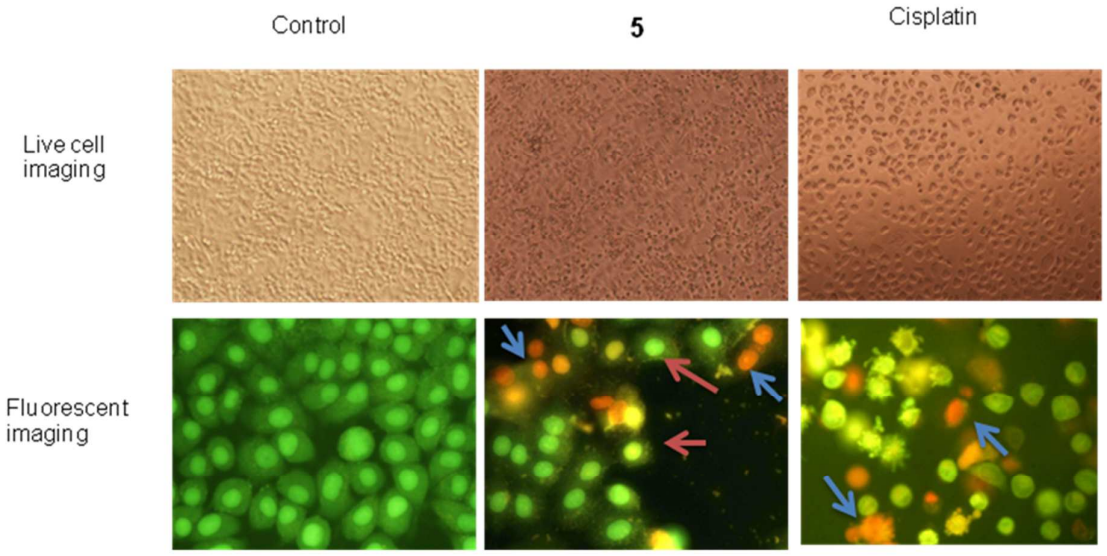


Fig. 7 Morphological observations of IC_{50} concentration of compound **1** and cisplatin treated lung (A549) cancer cells showing cell shrinkage, dead and floating cells by live cell imaging and early (red arrow indicating nuclear condensed bright yellowish green cells) and late (blue arrow indicating the DNA fragmentation and formation apoptotic bodies) apoptotic cells by fluorescent imaging.

Conclusions

In summary, we have described the successful synthesis of neutral molecular stirrup like rhenium(I)-based dinuclear metallacycles having ON∩NO chelation in a one-pot reaction under solvothermal conditions. Three precursor hetero-ligand self-assembly was facilitated by oxidative addition of N,N′-di(aryl)oxamide ligands to rhenium carbonyl in presence of ester functionalised flexible ditopic linkers via orthogonal bonding approach. Molecular structures of the metallacycles were determined by single crystal X-ray diffraction studies which revealed a dinuclear stirrup like skeletal framework with isostructural features. Anti-cancer activity of the compounds was probed against various cancer cell lines. Compound **1** in colon cancer cells and compound **5** in lung and colon cancer cells showed induction of apoptosis by live cell and florescent imaging. The compounds presumably induce apoptosis in cancer cells, which might contribute for the anticancer activity. The cytotoxicity studies have shed some light on structure-activity relation. Hence, on appropriate optimization in skeletal framework, this class of compounds may be promising anticancer compounds.

Experimental

Materials and Methods

All manipulations were carried out under dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. $Re_2(CO)_{10}$ was purchased from Sigma Aldrich. Oxamide ligands and ester functionalised flexible ligands were synthesized as reported in literature.[33] Mesitylene and other solvents were purified using standard methods and freshly distilled prior to use.[34] IR spectra were recorded on a Thermo Nicolet 6700 FT-IR Spectrometer. Electronic absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Emission spectra were recorded a Fluoromax-4 spectrofluorometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Elemental analyses were performed using Thermo Scientific Flash 2000 CHNS analyser.

Crystallographic Structure Determination

Structural studies were performed on CCD Oxford Diffraction XCALIBUR-EOS CCD equipped diffractometer, with an Oxford Instruments low-temperature attachment. Crystal data for compound **2**–**4** were collected at 120 K while data for **5** were collected at 150 K using graphite-monochromated Mo Kα radiation (λ_α = 0.7107 Å). The strategy for data collection was evaluated by using CrysAlisPro CCD software. The data were collected by standard 'ψ–ω scan' techniques, and were scaled and reduced using CrysAlisPro Version 1.171.36.21 software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97 refining on F^2.[35] The positions on all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 × U_{eq} of their parent atoms.

Synthesis of [(CO)$_3$Re(μ-dpo)(μ-pdi)Re(CO)$_3$] (1)

A mixture of $Re_2(CO)_{10}$ (65 mg, 0.1 mmol), N,N′-diphenyloxamide (24 mg, 0.1 mmol) and *o*-phenylene diisonicotinate (27 mg, 0.1 mmol) in mesitylene (6 mL) was taken in a 23 mL PTFE flask and sealed in a stainless steel solvothermal bomb. The bomb was placed in an oven maintained at 160 ˚C for 6 h and then cooled to room temperature. Yellow brown crystalline product was obtained. The crystals were separated, washed with hexane and dried under vacuum. Yield: 94 mg, 85 %. Calc. for $C_{38}H_{22}N_4O_{12}Re_2$: C, 41.53; H, 2.02; N, 5.10. Found: C, 42.89; H, 2.11; N, 4.94. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 2029 (s), 2022 (vs), 1918 (vs), 1904 (vs), $\nu_{(ester\ C=O)}$ 1763 (w), $\nu_{(amide\ C=O)}$ 1600 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.48 (dd, H^2, py, 4H), 7.87 (dd, H^3, py, 4H), 7.51 (m, H^2, H^4, Ph, 6H), 7.45 (m, $H^{2'}$, Ph, 2H), 7.32 (m, $H^{3'}$, Ph, 2H), 7.10 (m, H^2, Ph, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.1, 195.8, 194.3 ($Re(CO)_3$), 171.2 (amide CO), 161.7 (ester CO), 153.9 (C^2, py), 145.5 (C^4, py), 141.9, 137.7 (aromatic), 129.5 (C^3, py), 128.5, 126.5, 124.9, 124.6, 123.5

(aromatic). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 227 (41286), 267 (36431) (LIG), 332 (31080) (MLCT). Emission (CH_2Cl_2, nm): λ_{max}^{em} 436.

Synthesis of $[(CO)_3Re(\mu\text{-dbno})(\mu\text{-pdi})Re(CO)_3]$ (2)

A mixture of $Re_2(CO)_{10}$ (65 mg, 0.1 mmol), N,N′-dibenzyloxamide (27 mg, 0.1 mmol) and *o*-phenylene diisonicotinate (27 mg, 0.1 mmol) in mesitylene (6 mL) was taken in a 23 mL PTFE flask and sealed in a stainless steel solvothermal bomb. The bomb was placed in an oven maintained at 150 ˚C for 12 h and then cooled to room temperature. Yellow colour solution was obtained and mesitylene was removed by vacuum distillation. The reaction mixture was washed with hexane and chromatographed on a silica gel column using a solvent mixture of dichloromethane and hexane (4:1) as eluent. The product was isolated as a yellow solid. Yield: 96 mg, 86 %. Calcd. for $C_{40}H_{26}N_4O_{12}Re_2$: C, 42.63; H, 2.33; N, 4.97. Found: C, 43.49; H, 2.39; N, 4.78. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 2027 (s), 2020 (vs), 1916 (vs), 1895 (vs), $\nu_{(ester\ C=O)}$ 1762 (w), $\nu_{(amide\ C=O)}$ 1595 (s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.10 (dd, 4H, H^2, py), 7.50 (dd, 4H, H^3, py), 7.45 (m, 4H, Ph), 7.33 (m, 10H, Ph), 5.04 (d, 4H, benzyl), 4.67 (d, 4H, benzyl). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.3, 196.9, 194.5 ($Re(CO)_3$), 172.6 (amide CO), 161.6 (ester CO), 154.0 (C^2, py), 141.8 (C^4, py), 138.6, 136.9 (aromatic), 129.9 (C^3, py), 128.5, 128.3, 128.1, 124.3, 123.5 (aromatic), 55.4 (benzyl). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 227 (42077), 266 (35418) (LIG), 324 (31868) (MLCT). Emission (CH_2Cl_2, nm): λ_{max}^{em} 429.

Synthesis of $[(CO)_3Re(\mu\text{-dpo})(\mu\text{-etdp})Re(CO)_3]$ (3)

A mixture of $Re_2(CO)_{10}$ (65 mg, 0.1 mmol), N,N′-diphenyloxamide (24 mg, 0.1 mmol) and ethane diyl di-4-pyridine carboxylate (27 mg, 0.1 mmol) in mesitylene (6 mL) was taken in a 23 mL PTFE flask and sealed in a stainless steel solvothermal bomb. The bomb was placed in an oven maintained at 160 ˚C for 10 h and then cooled to room temperature. Yellow colour solution was obtained and mesitylene was removed by vacuum distillation. The reaction mixture was washed with hexane and chromatographed on a silica gel column using a solvent mixture of dichloromethane

and hexane (4:1) as eluent. The product was isolated as a bright yellow solid. Yield: 92 mg, 88 %. Calcd. for $C_{34}H_{22}N_4O_{12}Re_2$: C, 38.86; H, 2.11; N, 5.33. Found: C, 39.49; H, 2.19; N, 5.21. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 2029 (s), 2021 (vs), 1917 (vs), 1904 (vs), $\nu_{(ester\ C=O)}$ 1742 (w), $\nu_{(amide\ C=O)}$ 1600 (m). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.41 (dd, H^2, py, 4H), 7.71 (dd, 4H, H^3, py), 7.50 (m, 4H, H^1, Ph), 7.31 (m, 2H, H^3, Ph), 7.06 (m, 4H, H^2, Ph), 5.14 (m, 2H, CH_2), 4.66 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.2, 195.9, 194.4 ($Re(CO)_3$), 171.3 (amide CO), 163.2 (ester CO), 153.6 (C^2, py), 145.6 (C^4, py), 138.6 (aromatic), 129.5 (C^3, py), 126.4, 124.8, 124.3 (aromatic), 61.2 (CH_2). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 227 (40983), 267 (34660) (LIG), 337 (30892) (MLCT). Emission (CH_2Cl_2, nm): λ_{max}^{em} 585.

Synthesis of $[(CO)_3Re(\mu\text{-dbno})(\mu\text{-etdp})Re(CO)_3]$ (4)

A mixture of $Re_2(CO)_{10}$ (65 mg, 0.1 mmol), N,N′-dibenzyloxamide (27 mg, 0.1 mmol) and ethane diyl di-4-pyridine carboxylate (27 mg, 0.1 mmol) in mesitylene (6 mL) was taken in a 23 mL PTFE flask and sealed in a stainless steel solvothermal bomb. The bomb was placed in an oven maintained at 160 ˚C for 10 h and then cooled to room temperature. Yellow colour solution was obtained and mesitylene was removed by vacuum distillation. The reaction mixture was washed with hexane and chromatographed on a silica gel column using a solvent mixture of dichloromethane and hexane (4:1) as eluent. The product was isolated as a bright yellow solid. Yield: 90 mg, 85%. Calcd. for $C_{36}H_{26}N_4O_{12}Re_2$: C, 40.07; H, 2.43; N, 5.19. Found: C, 41.69; H, 2.37; N, 5.03. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 2029 (s), 2021 (vs), 1917 (vs), 1901 (vs), $\nu_{(ester\ C=O)}$ 1739 (w), $\nu_{(amide\ C=O)}$ 1601 (m). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (dd, 4H, H^2, py), 7.36 (dd, 4H, H^3, py), 7.32 (m, 6H, H^2, H^4, oxamidato Ph), 7.25 (m, 4H, H^3, oxamidato Ph), 5.19 (m, 2H, CH_2), 4.48 (m, 2H, CH_2), 4.98 (d, 2H, benzyl), 4.65 (d, 2H, benzyl). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.3, 197.0, 193.9 ($Re(CO)_3$), 172.6 (amide CO), 163.3 (ester CO), 153.7 (C^2, py), 138.6 (C^4, py), 137.9 (aromatic), 129.8 (C^3, py), 128.7, 128.0, 124.1 (aromatic), 61.5 (CH_2), 55.2 (benzyl CH_2). UV−vis (CH_2Cl_2,

λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 228 (42564), 269 (33560) (LIG), 340 (32190) (MLCT). Emission (CH_2Cl_2, nm): λ_{max}^{em} 421, 587.

Synthesis of [$(CO)_3$Re(μ-dpo)(μ-budp)Re$(CO)_3$] (5)

A mixture of $Re_2(CO)_{10}$ (65 mg, 0.1 mmol), N,N′-diphenyloxamide (24 mg, 0.1 mmol) and 1,4-butane diyl di-4-pyridine carboxylate (30 mg, 0.1 mmol) in mesitylene (6 mL) was taken in a 23 mL PTFE flask and sealed in a stainless steel solvothermal bomb. The bomb was placed in an oven maintained at 160 °C for 13 h and then cooled to room temperature. Yellow crystalline product was obtained. The crystals were separated, washed with hexane and dried under vacuum. Yield: 85 mg, 80 %. Calcd. for $C_{36}H_{26}N_4O_{12}Re_2$: C, 40.07; H, 2.43; N, 5.19. Found: C, 41.58; H, 2.36; N, 5.08. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 2029 (s), 2022 (vs), 1917 (vs), 1904 (vs), $\nu_{(ester\ C=O)}$ 1735 (w), $\nu_{(amide\ C=O)}$ 1601 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.41 (d, 4H, H^2, py), 7.73 (dd, 4H, H^3, py), 7.47 (t, 4H, H^2, Ph), 7.28 (m, 2H, H^4, Ph), 7.08 (d, 4H, H^3, Ph), 4.56 (m, 4H, OCH_2), 2.10 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.3, 196.0, 194.3 ($Re(CO)_3$), 171.5 (amide CO), 163.1 (ester CO), 153.3 (C^2, py), 145.9 (C^4, py), 139.5 (C^1, Ph), 129.4 (C^3, py), 126.4 (C^4, Ph), 124.6 (C^2, Ph), 124.5 (C^3, Ph), 65.8 (OCH_2), 25.9 (CH_2). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 229 (41830), 267 (35203) (LIG), 340 (29880) (MLCT).

Cell culture and cytotoxicity assay

Lung (A549), cervical (HeLa) and colon (HCT-15) cancer cell lines were obtained from NCCS (National Centre for Cell Science) Pune, India. The cancer cell lines-A549 and HeLa were maintained in Dulbecco's Modified Eagle Medium (DMEM) while HCT-15 was maintained in Roswell Park Memorial Institute (RPMI-1640) media supplemented with 10% Fetal bovine serum (FBS), 10 U/ml of penicillin, 10 mg/L of streptomycin, and 0.25 mg/L of amphotericin B at 37 °C

and 5% CO_2 incubator. MTT assay was performed as described in the literature[16b] with slight modifications and the details pertaining to cytotoxicity assay are given in supporting information.

Morphological observations of cancer cells treated with compound 1 and 5

The morphological observation of compound **1** in colon (HCT-15) and compound **5** in lung (A549) and colon (HCT-15) treated cancer cells was done by live cell and fluorescent imaging. For live cell imaging, the cancer cells were treated with respective IC_{50} value of compounds (control cells received 0.05% DMSO) for 48 h and observed under phase contrast microscope. For fluorescent imaging, the cancer cells after treating with respective IC_{50} value of compounds for 48 h, were stained with acridine orange-ethidium bromide (1 μg/ml) and observed under fluorescent microscope.

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Electronic Supplementary Information (ESI) available: The crystallographic data and structure refinement details of **2**–**5**, Experimental details of cytotoxic studies and graphical representation of cytotoxicity of compounds **1**–**5** against different cell lines. This material is available free of charge via the internet at http:// pubs.acs.org.

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