Electronic Supplementary Material (ESI) for CrystEngComm.

Supramolecular Assembly Through Intermolecular n → π* Interactions by Coordinated Perrhenate Formed *via* Superoxidation of Re(I) in $Re(CO)_3$ Complexes Bearing Diimine Ligands

Reza Kia,*[a] Tahereh Taghavi[a] and Paul R. Raithby[b]

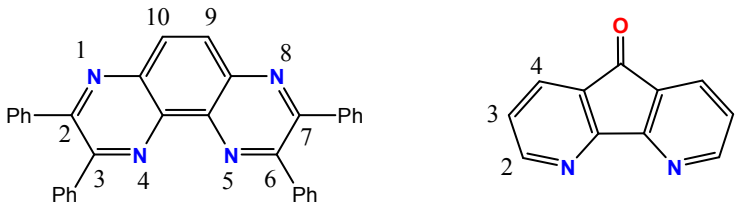
[a]*Chemistry Department, Sharif University of Technology, P.O. Box 11155-3516, Tehran, Iran. E-mail: rkia@sharif.edu & zsrkk@yahoo.com*

[b]*Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK*

1. Experimental

1.1. Materials, methods and instrumentation

All reagents were purchased from Aldrich and used as received. All solvents were reagent grade and purified by standard techniques where required. The 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenantherene ligand (Ph_4TAP) was synthesized by a reported procedure [1]. Infrared spectra in the region of 500-4000 cm^{-1} and 600-4000 cm^{-1} were recorded in KBr discs with a Bruker IFD 25 FT-IR and as a neat sample with a Perkin Elmer spectrum 100FT-IR ATR spectrometer for **1** and **2**, respectively. The ^{1}H-NMR spectra were recorded by Bruker Avance 500 MHz spectrometer. The elemental analyses were done by a LECO CHNO analyser. The ESI-MS spectra were recorded by micro-TOF Bruker in methanol.



Chemical scheme of **Ph_4TAP** (left) and **Dafone** (right)

^{1}H-NMR of **Ph_4TAP** ($CDCl_3$, σ_{ppm}): 7.36-7.44 (8H, hydrogen of the phenyl substituents in *meta*- & *para*-positions); 7.66-7.77 (8H, ortho-positions of the phenyl rings); 8.18 (2H, H^9 & H^{10}.

1H-NMR of **Dafone** ($CDCl_3$, σ_{ppm}): 7.26-7.37 (H^3); 7.97-8.01 (H^4); 8.78-8.81 (H^2).

1.2. Synthesis and crystallization of 1 & 2

An equimolar quantity of $Re(CO)_5Br$ (203 mg, 0.5 mmol) and Ph_4TAP (243 mg, 0.5 mmol) or Dafone (91 mg, 0.5 mmol) were mixed and refluxed in toluene (40 mL) for 8 h in air. Each reaction was repeated several times and consistent yields of the products were obtained. The orange precipitate was obtained by adding *n*-hexane to the concentrated solution. Single-crystals suitable for X-ray analysis were grown by vapor diffusion of *n*-hexane into dichloromethane solution of **1** and **2**. Different parts of the single-crystal batch was selected, ground and heated in vacuum oven for CHNO analysis by averaging two data sets of elemental analyses.

(1) Yield (351 mg, 69%). Elemental analyses, *Calc*. (%): C, 44.13; H, 2.20; N, 5.56; O, 11.12 *Found*: C, 44.11; H, 2.20; N, 5.58; O, 11.10. ^{1}H-NMR ($CDCl_3$, σ_{ppm}): 7.12-7.98 (20H, hydrogen of phenyl substituents in 2, 3, 6, and 7 position of the tetraazaphenantherene base); 8.56 (2H, H^9 & H^{10}). FTIR (KBr, cm^{-1}): 2029, 1938 and 1901 (CO stretching).

(2) Yield (248 mg, 70%). Elemental analyses, *Calc*. (%): C, 23.93; H, 0.86; N, 3.99; O, 18.22 *Found*: C, 23.90; H, 0.86; N, 4.01; O, 18.23. ^{1}H-NMR ($CDCl_3$, σ_{ppm}): 7.67-7.70 (2H, H^3); 8.20-8.23 (2H, H^4); 8.89-8.91 (2H, H^2). FTIR (ATR, cm^{-1}): 2018 and 1893 (CO stretching).

2. Computational details

Density functional theory (DFT) calculations have been performed using the *Gaussian 09* package to perform geometry optimizations, the vibrational frequencies and the electronic structures of the complex [2]. A frequency calculation after each geometry optimization ensured that the calculated structures are real minima in the potential energy surface of the molecules. The structure was optimized using the B3LYP exchange-correlation functionals with the LANL2DZ effective core pseudo-potential (ECP) and corresponding set of basic functions for Re and 6-31G* (five pure d functions) for C, H, N and O [3]. The NBO program [4] embedded in Gaussian 09 package used for calculations was done at B3LYP/LANL2DZ level of theory on optimized molecule. The natural bond orbital analysis emphasizes the role of intra- and intermolecular interaction or charge transfer in the title compound. It is performed by including all possible interaction between filled donor and empty acceptor NBOs and estimating the energetic importance by second-order perturbation theory.

3. X-ray crystallography

Single crystals of **1** and **2** suitable for X-ray diffraction analysis, were grown by slow vapor diffusion of *n*-hexane into dichloromethane solution of the complex. Details of the crystal data collection and refinement parameters are summarized in Table S1-S2. X-ray intensity data were collected using the full sphere routine by φ and ω scans strategy on the Agilent *SuperNova* dual wavelength EoS *S*2 diffractometer with mirror monochromated Mo K*α* radiation (λ = 0.71073

Å). For all data collections the crystals were cooled to 150(2) K using an Oxford Diffraction Cryojet low-temperature attachment. The data reduction, including an empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm [5], was performed using the *CrysAlisPro* software package [6]. The crystal structures were solved by direct methods using the online version of *AutoChem 2.0* in conjunction with *OLEX2* [7] suite of programs implemented in the *CrysAlis* software, and then refined by full-matrix least-squares (*SHELXL2014*) on F^2 [8]. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were positioned geometrically in idealized positions and refined with the riding model approximation, with U_{iso}(H) = 1.2 U_{eq}(C). For the molecular graphics the program SHELXTL was used [8]. All geometric calculations were carried out using the *PLATON* software [9]. In complex **1** the Re atom was disordered over two positions with a refined site occupancy ratio of 0.937(2)/0.063(2). The complex **1** also contains solvent accessible voids of 879 Å^3, equals to 189 electrons in its unit cell. This fits well to four molecules of *n*-hexane in the unit cell. Since the solvent was not modelled explicitly the contribution of its electron density was subtracted from the structure by back Fourier transform using the *SQUEEZE* routine in *PLATON*. The contribution of the solvent molecules were included in the CIF file [through SFAC in the refinement and in the resulted new *F(000)*, molecular weight, density, and linear absorption coefficient]. The new modified CIF file was also deposited in the designated CCDC webpage with the same CCDC umber 2013747 as a revised CIF.

CCDC **2013747-2013748** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

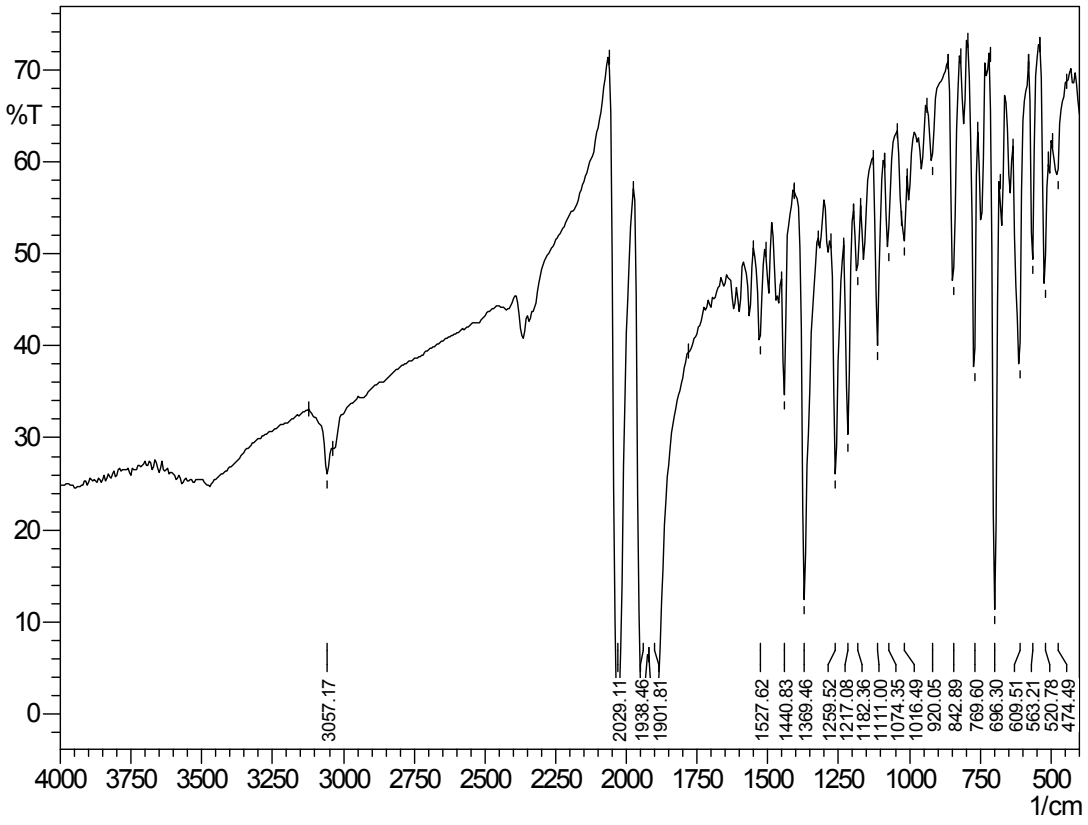


Fig. S1. The FT-IR spectrum of **1**.

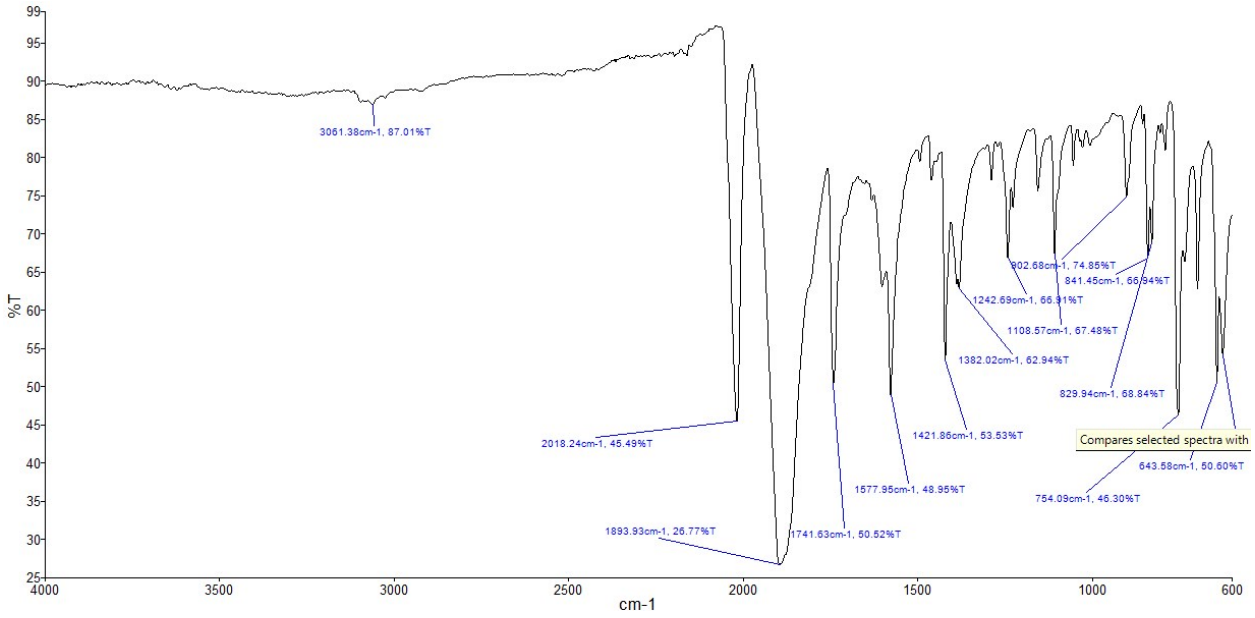


Fig. S2. The FT-IR (ATR) spectrum of **2**.

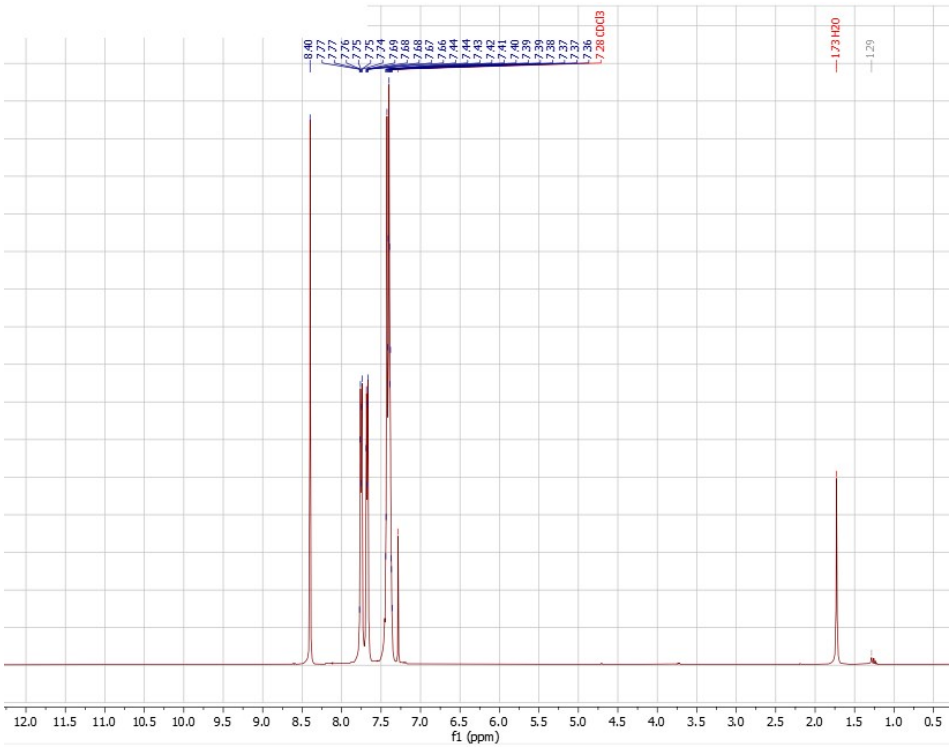


Figure S3. ^{1}H NMR (500 MHz) spectrum of Ph_4TAP in $CDCl_3$.

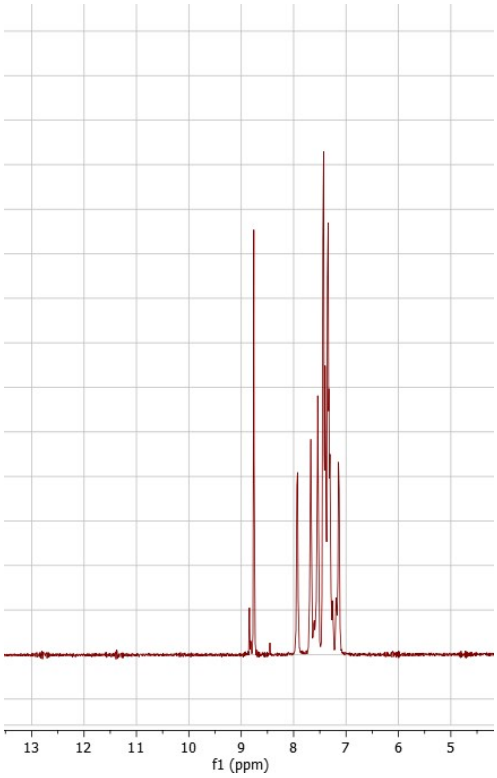


Figure S4. ^{1}H NMR (500 MHz) spectrum of **1** in $CDCl_3$.

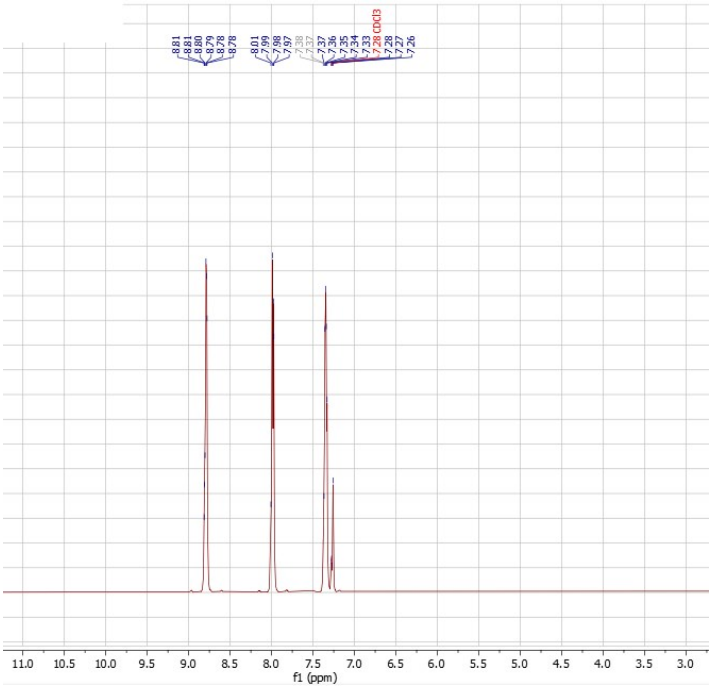


Figure S5. ^{1}H NMR (500 MHz) spectrum of Dafone in $CDCl_3$.

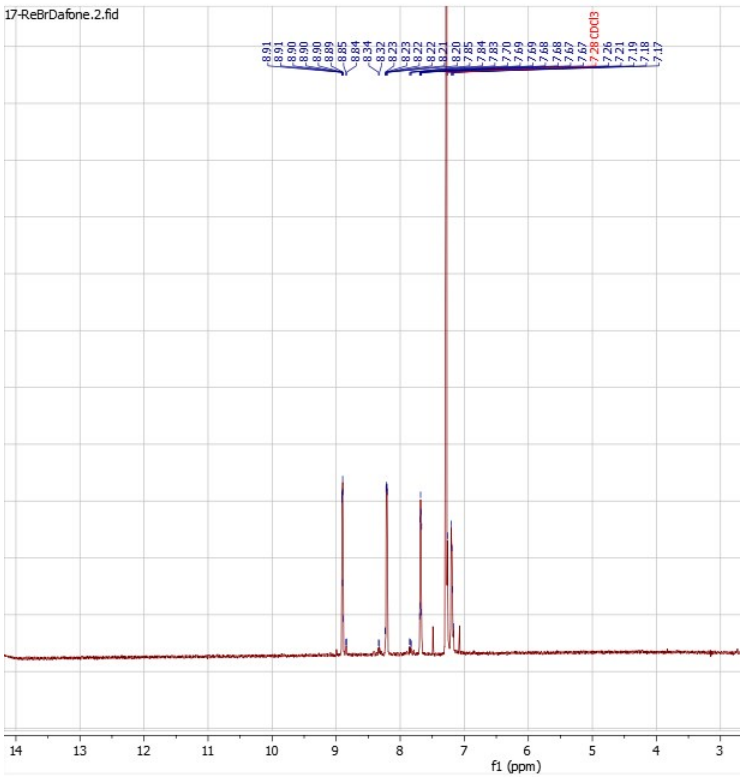


Figure S6. ^{1}H NMR (500 MHz) spectrum of **2** in $CDCl_3$.

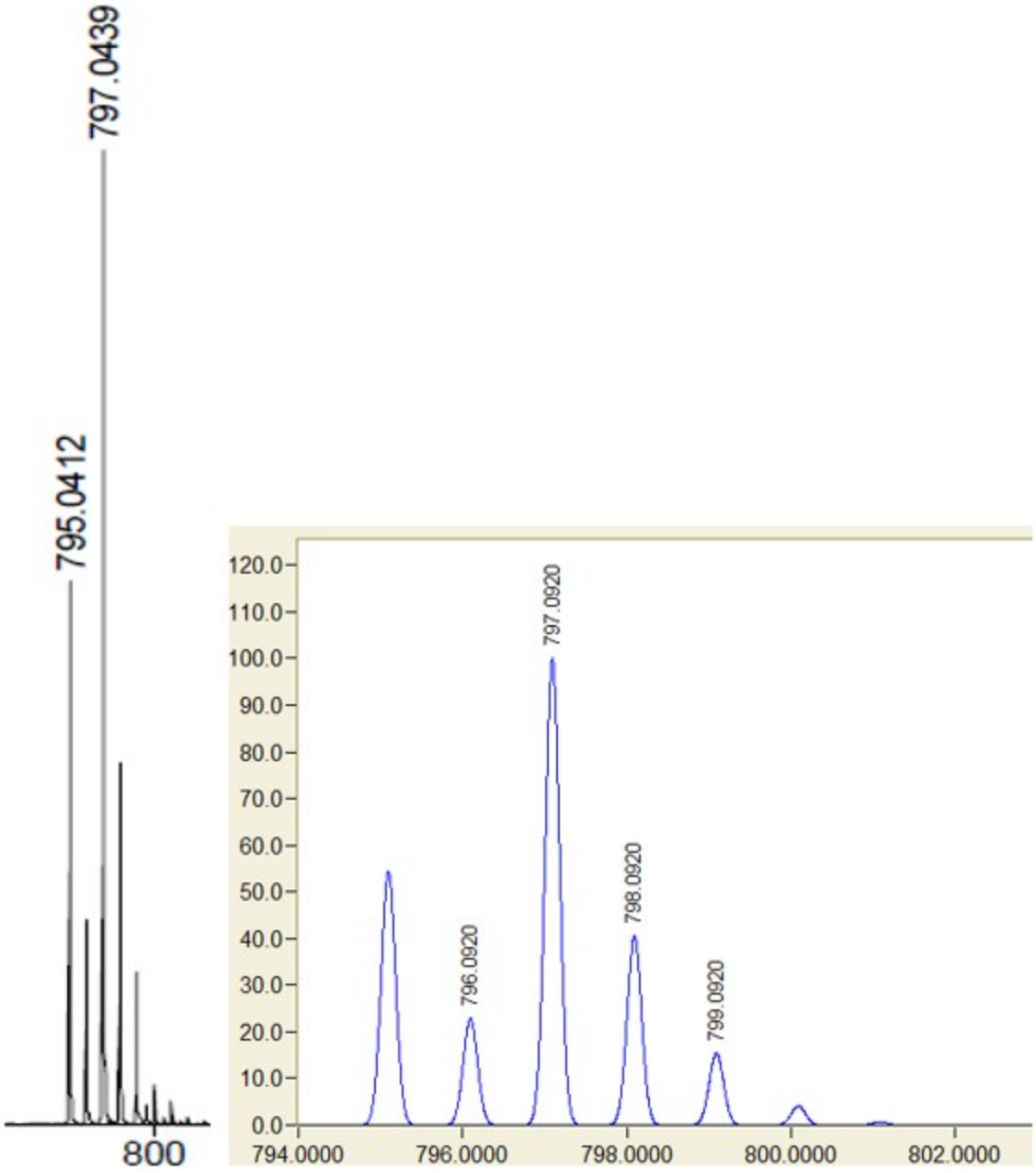


Fig. S7. The ESI-MS spectrum of **1** wit base peak at m/z = 797.0439 (left) and the simulated one.

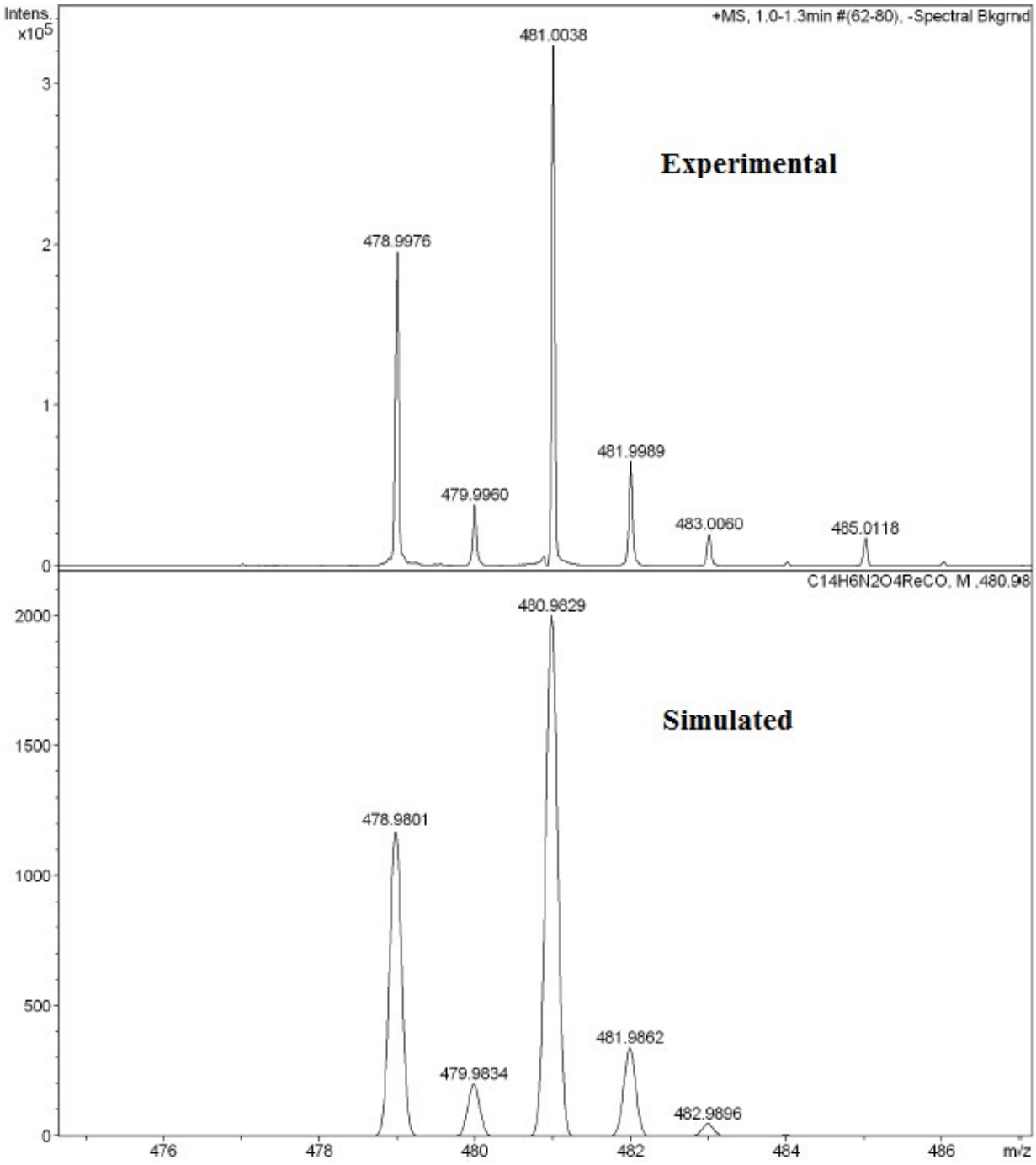


Fig. S8. The ESI-MS spectrum of **2** with base peak of $[Re(Dafone)(CO)_4]^+$ at m/z = 481.0038.

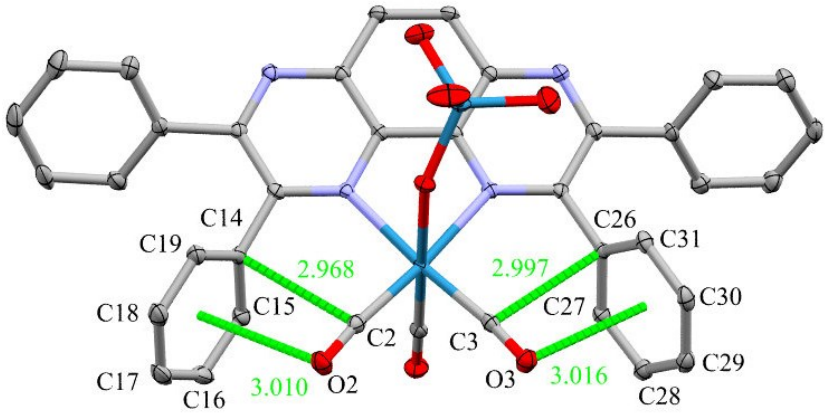


Figure S9. The intramolecular π→π and n→π* interactions in **1** through π(*Cg*1)···π*(C2≡O2), π(*Cg*2)···π*(C3≡O3), O2···*Cg*1, and O3···*Cg*2. *Cg1* and *Cg2* are centroids of C14-C19 and C26-C31, respectively.

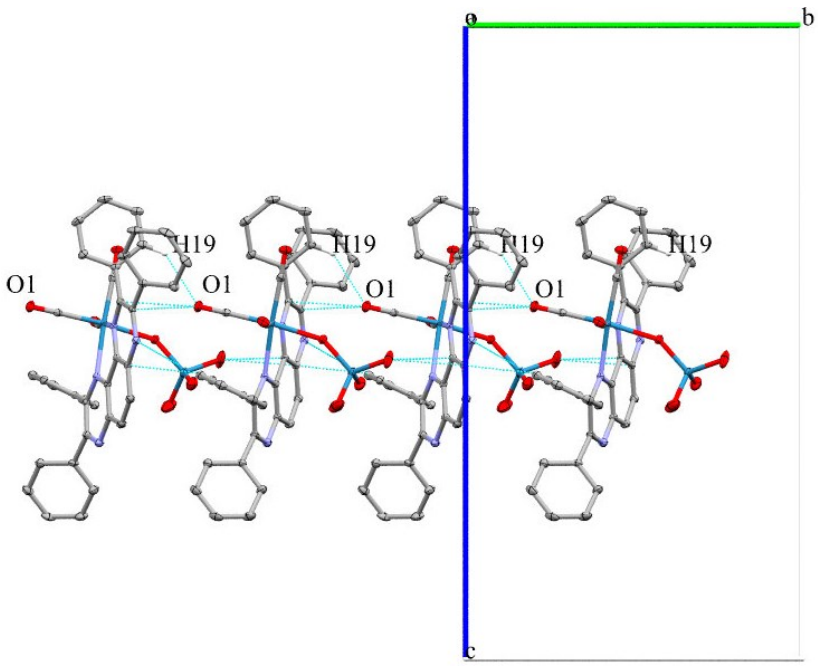


Figure S10. The crystal packing of **1** showing an extended chain along the *b*-axis through C−H···O and n→π* interactions. Only the involved H atoms are shown.

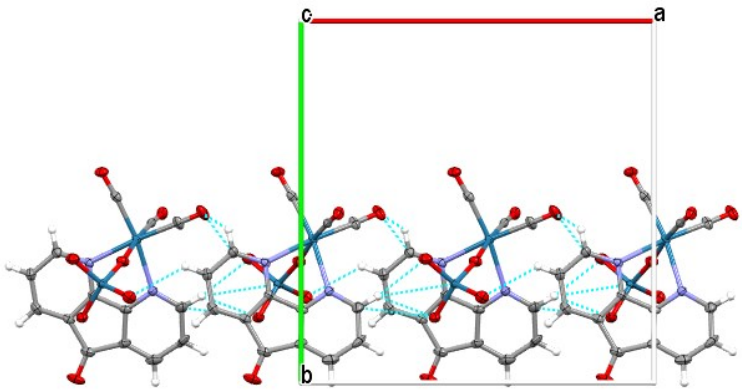


Fig. S11. The crystal packing of **2** was also consolidated by intermolecular C–H···O interactions along the *a*-axis.

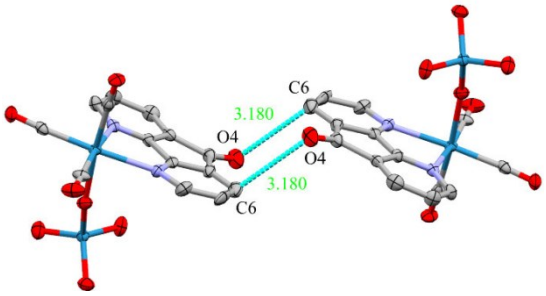


Figure S12. The formed dimer of **2** through centrosymmetric n→π* interactions of C=O···π*.

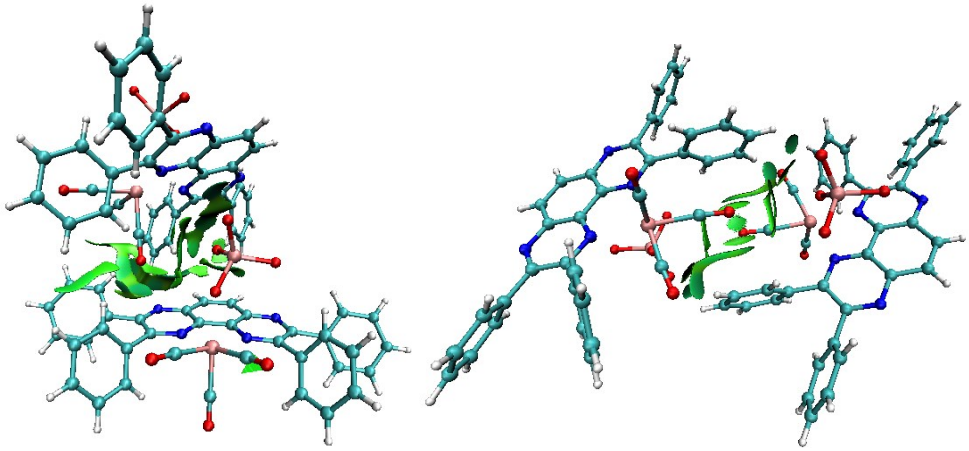


Fig. S13. The NCI plot of the dimers of **1**.

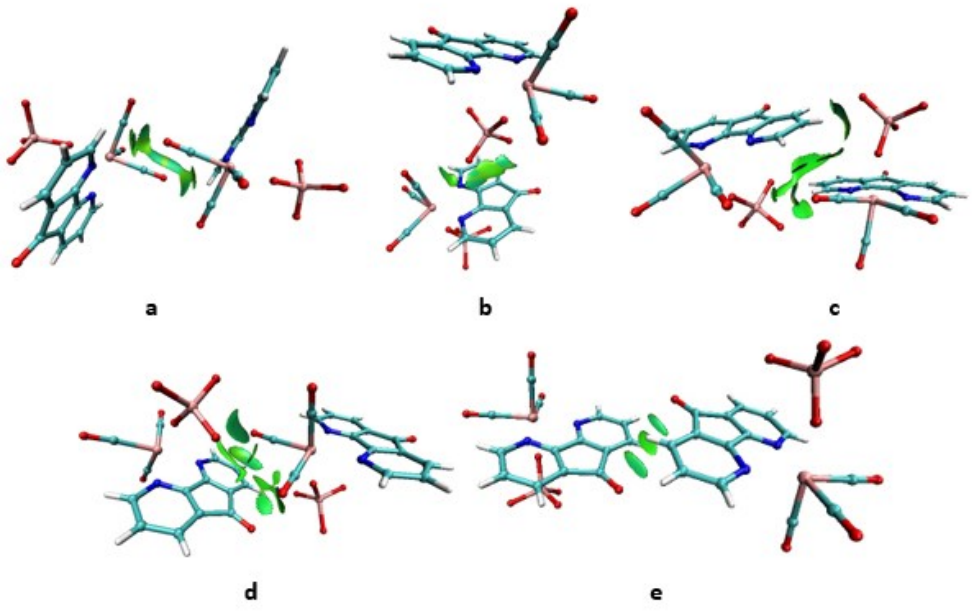


Fig. S13. The NCI plot of the dimers of **2**.

The optimized geometry of **1**

Re	-0.87962600	-1.40067200	2.40257300
O	0.07584600	-0.08164300	1.67204700
O	-0.20633700	-2.90855900	1.91029800
O	-0.83897700	-1.27695500	4.11566000
O	-2.50984600	-1.30834800	1.84112500
Re	0.24106600	1.44109800	0.13859800
N	2.94364200	-2.51177100	-1.38777000
N	-1.14347000	0.00041100	-0.93405100
O	-1.80046500	3.25462700	1.57331700
C	-1.07244700	2.55946600	1.00272000
N	1.63897800	-0.11470000	-0.75302700
C	0.93580600	-1.22542400	-1.12114800
C	-0.48973400	-1.16715700	-1.21581400
C	3.63812100	-1.41130900	-1.12633600
C	-4.15823200	1.30432400	0.24228200
H	-4.28736900	0.42142500	0.86045200

N	-2.54424000	-2.29315200	-1.73408400
C	1.59892300	-2.44218000	-1.40228600
C	-4.70671500	3.59933900	-0.29565300
H	-5.28481800	4.49788700	-0.09872600
C	-3.02451100	2.43374600	-1.58366700
H	-2.30047400	2.42215200	-2.39293900
C	-3.77324700	3.58396900	-1.33424600
H	-3.62315300	4.46706700	-1.94879600
C	-3.21623500	1.28691000	-0.79753700
C	3.77195800	1.02775900	-0.41166000
C	2.97993500	-0.17729200	-0.77154900
C	-4.89164600	2.46225000	0.49434900
H	-5.60623500	2.47649100	1.31213200
C	5.69199500	-2.74213200	-0.69705500
H	5.05117800	-3.47466500	-0.21729600
C	1.52759500	2.43446600	1.17785300
C	5.11789900	-1.56715300	-1.21128700
C	3.70995900	2.18126900	-1.20915800
H	3.05607300	2.20540400	-2.07524900
C	0.84478100	-3.61596500	-1.73323700
H	1.40169700	-4.52789500	-1.91866400
C	-0.51167900	-3.55961700	-1.82226200
H	-1.11288900	-4.42407200	-2.08199100
C	-1.20587400	-2.32729000	-1.58410800
C	-5.33444200	-0.20707800	-2.49544100
H	-4.80378200	0.65857000	-2.87601600
C	5.94509900	-0.63457900	-1.85772600
H	5.52134300	0.26875700	-2.28200800
C	4.63142000	1.00134500	0.69664100
H	4.68873800	0.10966200	1.31367400

C	-4.64867800	-1.19182000	-1.76659800
C	7.06307100	-2.96520300	-0.80083800
H	7.49376100	-3.87176200	-0.38498100
C	-5.35664900	-2.31417400	-1.30467900
H	-4.82374100	-3.08043500	-0.75167300
C	-6.72332600	-2.43574700	-1.54449900
H	-7.26098600	-3.30084700	-1.16666900
C	5.40053200	2.11924300	1.01331000
H	6.04866400	2.09599000	1.88442400
C	-7.39803000	-1.45104600	-2.27010700
H	-8.46323700	-1.54796100	-2.46171700
C	5.33750900	3.26362100	0.21520300
H	5.94206400	4.13195400	0.46136200
C	7.31398500	-0.87017800	-1.97657600
H	7.93920800	-0.14489900	-2.48971200
C	-6.69830400	-0.34221400	-2.75028100
H	-7.21390000	0.42177900	-3.32543000
C	4.49474100	3.29152500	-0.89788700
H	4.44204800	4.17843000	-1.52279000
C	7.87868500	-2.02985700	-1.44200700
H	8.94750600	-2.20552700	-1.52793800
C	-2.47370800	0.03534700	-1.09461600
C	-3.17901700	-1.14728200	-1.53267100
O	2.24490800	3.05270900	1.84367900
O	0.46559600	3.39819600	-2.22012200
C	0.38548000	2.67092700	-1.31189000

The optimized geometry of **2**

C	3.01298900	1.33980200	0.60483000
C	2.90115800	-0.58291100	-1.33682400
C	2.51074100	-1.25932900	1.29752500
C	0.56430100	1.85779500	-2.51403300
H	1.36527600	1.45684000	-3.12511300
C	-0.39202500	2.72673300	-3.04781800
H	-0.31857300	2.99822000	-4.09539100
C	-1.43684000	3.23471900	-2.25401600
H	-2.18818000	3.90133000	-2.66592300
C	-1.46155900	2.83017900	-0.92733900
C	-0.45921100	1.96548900	-0.49914300
C	-0.65564800	1.61844400	0.89130400
C	-1.78928600	2.24935900	1.39212200
C	-2.14319700	1.98389800	2.70775500
H	-3.02007800	2.42852200	3.16801200
C	-1.31655700	1.09247600	3.41490300
H	-1.54528900	0.83124700	4.44230600
C	-0.19974500	0.50740200	2.81070500
H	0.42831700	-0.19456000	3.34696000
C	-2.37960000	3.07714100	0.26074000
N	0.54316900	1.46669100	-1.21859200
N	0.15078100	0.77259800	1.53017600
O	3.76225800	2.16768400	0.92845400
O	3.58658700	-0.92438000	-2.20634000
O	2.95474700	-2.01988800	2.04998200
O	-3.35922600	3.78449900	0.29871100
Re	1.73715100	0.00949500	0.07554100
O	0.16704300	-1.34037000	-0.53538600
O	-1.99071000	-3.00982200	-1.41622300

O	-1.82833500	-2.26537500	1.30096000
O	-2.50429600	-0.34571400	-0.61973100
Re	-1.55604100	-1.76038700	-0.32166900

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	C40 H29 N4 O7 Re2	
Formula weight	1050.07	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbcn*	
Unit cell dimensions	*a* = 20.7375(11) Å	α= 90°
	b = 13.4812(7) Å	β= 90°
	c = 25.4131(13) Å	γ = 90°
Volume	7104.6(6) Å^3	
Z	8	
Density (calculated)	1.963 Mg/m^3	
Absorption coefficient	6.867 mm^{-1}	
F(000)	4024	
Crystal size	0.080 x 0.050 x 0.020 mm^3	
Theta range for data collection	1.880 to 30.582°	
Index ranges	-29<=h<=29, -19<=k<=19, -36<=l<=36	
Reflections collected	119706	
Independent reflections	10886 [R(int) = 0.0524]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. & min. transmission	1.0000 and 0.8920	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10886 / 0 / 461	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2 σ(I)]	R1 = 0.0210, wR2 = 0.0439	
R indices (all data)	R1 = 0.0308, wR2 = 0.0472	
Largest diff. peak and hole	0.767 and -0.816 e. Å^{-3}	

Table 2. Bond lengths [Å] and angles [°] for 1.

Re(1)-C(1)	1.892(2)
Re(1)-C(2)	1.911(3)
Re(1)-C(3)	1.935(2)
Re(1)-O(4)	2.1520(16)
Re(1)-N(2)	2.2016(19)
Re(1)-N(1)	2.2053(19)
N(3)-C(5)	1.323(3)
N(3)-C(6)	1.354(3)
N(2)-C(12)	1.336(3)
N(2)-C(8)	1.368(3)
O(3)-C(3)	1.142(3)
N(1)-C(4)	1.334(3)
N(1)-C(7)	1.360(3)
C(7)-C(6)	1.404(3)
C(7)-C(8)	1.424(3)
C(8)-C(9)	1.397(3)
C(5)-C(4)	1.438(3)
C(5)-C(20)	1.483(3)
C(31)-C(26)	1.393(3)
C(31)-C(30)	1.394(3)
C(31)-H(31)	0.9500
N(4)-C(13)	1.325(3)
N(4)-C(9)	1.355(3)
C(6)-C(11)	1.419(3)
C(29)-C(30)	1.381(4)
C(29)-C(28)	1.393(3)
C(29)-H(29)	0.9500
C(27)-C(28)	1.389(3)
C(27)-C(26)	1.391(3)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(26)-C(12)	1.483(3)
C(14)-C(15)	1.392(3)
C(14)-C(19)	1.399(3)

C(14)-C(4)	1.480(3)
C(30)-H(30)	0.9500
C(25)-C(24)	1.386(4)
C(25)-C(20)	1.396(3)
C(25)-H(25)	0.9500
C(2)-O(2)	1.156(3)
C(20)-C(21)	1.393(3)
C(15)-C(16)	1.390(3)
C(15)-H(15)	0.9500
C(11)-C(10)	1.355(3)
C(11)-H(11)	0.9500
C(10)-C(9)	1.427(3)
C(10)-H(10)	0.9500
C(33)-C(34)	1.384(3)
C(33)-C(32)	1.393(3)
C(33)-H(33)	0.9500
C(21)-C(22)	1.390(4)
C(21)-H(21)	0.9500
C(19)-C(18)	1.391(3)
C(19)-H(19)	0.9500
C(32)-C(37)	1.388(3)
C(32)-C(13)	1.488(3)
C(24)-C(23)	1.386(4)
C(24)-H(24)	0.9500
C(37)-C(36)	1.384(4)
C(37)-H(37)	0.9500
C(36)-C(35)	1.381(4)
C(36)-H(36)	0.9500
C(18)-C(17)	1.379(4)
C(18)-H(18)	0.9500
C(35)-C(34)	1.377(4)
C(35)-H(35)	0.9500
C(17)-C(16)	1.382(4)
C(17)-H(17)	0.9500
C(22)-C(23)	1.382(4)
C(22)-H(22)	0.9500

C(34)-H(34)	0.9500
C(16)-H(16)	0.9500
Re(2)-O(7)	1.709(2)
Re(2)-O(6)	1.709(2)
Re(2)-O(5)	1.7170(19)
Re(2)-O(4)	1.7628(17)
O(4)-Re(2A)	1.649(3)
O(5)-Re(2A)	1.837(5)
O(6)-Re(2A)	1.429(4)
O(7)-Re(2A)	2.308(11)
C(23)-H(23)	0.9500
C(12)-C(13)	1.422(3)
O(1)-C(1)	1.152(3)

C(1)-Re(1)-C(2)	89.05(10)
C(1)-Re(1)-C(3)	90.13(10)
C(2)-Re(1)-C(3)	82.97(10)
C(1)-Re(1)-O(4)	174.20(8)
C(2)-Re(1)-O(4)	95.53(8)
C(3)-Re(1)-O(4)	93.95(8)
C(1)-Re(1)-N(2)	94.27(8)
C(2)-Re(1)-N(2)	175.16(9)
C(3)-Re(1)-N(2)	100.53(8)
O(4)-Re(1)-N(2)	80.95(7)
C(1)-Re(1)-N(1)	94.54(8)
C(2)-Re(1)-N(1)	99.53(8)
C(3)-Re(1)-N(1)	174.73(8)
O(4)-Re(1)-N(1)	81.22(7)
N(2)-Re(1)-N(1)	76.71(7)
C(5)-N(3)-C(6)	117.91(19)
C(12)-N(2)-C(8)	117.33(19)
C(12)-N(2)-Re(1)	130.31(15)
C(8)-N(2)-Re(1)	112.10(14)
O(3)-C(3)-Re(1)	173.8(2)
C(4)-N(1)-C(7)	117.51(19)
C(4)-N(1)-Re(1)	130.14(15)

C(7)-N(1)-Re(1)	111.94(14)
N(1)-C(7)-C(6)	121.9(2)
N(1)-C(7)-C(8)	118.9(2)
C(6)-C(7)-C(8)	119.2(2)
N(2)-C(8)-C(9)	121.7(2)
N(2)-C(8)-C(7)	118.5(2)
C(9)-C(8)-C(7)	119.9(2)
N(3)-C(5)-C(4)	122.0(2)
N(3)-C(5)-C(20)	116.3(2)
C(4)-C(5)-C(20)	121.6(2)
C(26)-C(31)-C(30)	119.5(2)
C(26)-C(31)-H(31)	120.3
C(30)-C(31)-H(31)	120.3
C(13)-N(4)-C(9)	117.0(2)
N(3)-C(6)-C(7)	120.4(2)
N(3)-C(6)-C(11)	119.5(2)
C(7)-C(6)-C(11)	120.1(2)
C(30)-C(29)-C(28)	120.2(2)
C(30)-C(29)-H(29)	119.9
C(28)-C(29)-H(29)	119.9
C(28)-C(27)-C(26)	120.1(2)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(27)-C(28)-C(29)	119.7(2)
C(27)-C(28)-H(28)	120.1
C(29)-C(28)-H(28)	120.1
C(27)-C(26)-C(31)	120.1(2)
C(27)-C(26)-C(12)	120.7(2)
C(31)-C(26)-C(12)	119.1(2)
C(15)-C(14)-C(19)	119.6(2)
C(15)-C(14)-C(4)	119.4(2)
C(19)-C(14)-C(4)	120.9(2)
N(1)-C(4)-C(5)	120.1(2)
N(1)-C(4)-C(14)	119.2(2)
C(5)-C(4)-C(14)	120.7(2)
C(29)-C(30)-C(31)	120.3(2)

C(29)-C(30)-H(30)	119.8
C(31)-C(30)-H(30)	119.8
C(24)-C(25)-C(20)	120.3(2)
C(24)-C(25)-H(25)	119.8
C(20)-C(25)-H(25)	119.8
O(2)-C(2)-Re(1)	174.6(2)
C(21)-C(20)-C(25)	119.1(2)
C(21)-C(20)-C(5)	122.1(2)
C(25)-C(20)-C(5)	118.7(2)
C(16)-C(15)-C(14)	120.0(2)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(10)-C(11)-C(6)	120.5(2)
C(10)-C(11)-H(11)	119.7
C(6)-C(11)-H(11)	119.7
C(11)-C(10)-C(9)	120.7(2)
C(11)-C(10)-H(10)	119.6
C(9)-C(10)-H(10)	119.6
N(4)-C(9)-C(8)	120.9(2)
N(4)-C(9)-C(10)	119.5(2)
C(8)-C(9)-C(10)	119.6(2)
C(34)-C(33)-C(32)	119.5(2)
C(34)-C(33)-H(33)	120.2
C(32)-C(33)-H(33)	120.2
C(22)-C(21)-C(20)	120.0(3)
C(22)-C(21)-H(21)	120.0
C(20)-C(21)-H(21)	120.0
C(18)-C(19)-C(14)	119.7(2)
C(18)-C(19)-H(19)	120.2
C(14)-C(19)-H(19)	120.2
C(37)-C(32)-C(33)	119.6(2)
C(37)-C(32)-C(13)	119.8(2)
C(33)-C(32)-C(13)	120.5(2)
C(23)-C(24)-C(25)	120.3(3)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9

C(36)-C(37)-C(32)	119.9(2)
C(36)-C(37)-H(37)	120.0
C(32)-C(37)-H(37)	120.0
C(35)-C(36)-C(37)	120.5(2)
C(35)-C(36)-H(36)	119.8
C(37)-C(36)-H(36)	119.8
C(17)-C(18)-C(19)	120.2(2)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(34)-C(35)-C(36)	119.5(2)
C(34)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2
C(18)-C(17)-C(16)	120.5(2)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(23)-C(22)-C(21)	120.6(3)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(35)-C(34)-C(33)	120.9(2)
C(35)-C(34)-H(34)	119.6
C(33)-C(34)-H(34)	119.6
C(17)-C(16)-C(15)	120.0(2)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
O(7)-Re(2)-O(6)	109.73(13)
O(7)-Re(2)-O(5)	108.98(11)
O(6)-Re(2)-O(5)	108.76(10)
O(7)-Re(2)-O(4)	109.90(9)
O(6)-Re(2)-O(4)	109.36(10)
O(5)-Re(2)-O(4)	110.08(9)
Re(2A)-O(4)-Re(1)	167.7(3)
Re(2)-O(4)-Re(1)	148.70(10)
C(22)-C(23)-C(24)	119.6(2)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
N(2)-C(12)-C(13)	119.9(2)

N(2)-C(12)-C(26)	119.8(2)
C(13)-C(12)-C(26)	120.2(2)
N(4)-C(13)-C(12)	123.0(2)
N(4)-C(13)-C(32)	116.1(2)
C(12)-C(13)-C(32)	120.9(2)
O(1)-C(1)-Re(1)	178.1(2)
O(6)-Re(2A)-O(4)	133.8(3)
O(6)-Re(2A)-O(5)	116.48(18)
O(4)-Re(2A)-O(5)	109.7(3)
O(6)-Re(2A)-O(7)	93.9(4)
O(4)-Re(2A)-O(7)	90.2(4)
O(5)-Re(2A)-O(7)	83.8(4)

Table 3. Torsion angles [°] for **1**.

C(4)-N(1)-C(7)-C(6)	2.8(3)
Re(1)-N(1)-C(7)-C(6)	-170.66(17)
C(4)-N(1)-C(7)-C(8)	-175.6(2)
Re(1)-N(1)-C(7)-C(8)	11.0(3)
C(12)-N(2)-C(8)-C(9)	-3.2(3)
Re(1)-N(2)-C(8)-C(9)	171.51(17)
C(12)-N(2)-C(8)-C(7)	176.2(2)
Re(1)-N(2)-C(8)-C(7)	-9.1(2)
N(1)-C(7)-C(8)-N(2)	-1.4(3)
C(6)-C(7)-C(8)-N(2)	-179.7(2)
N(1)-C(7)-C(8)-C(9)	178.0(2)
C(6)-C(7)-C(8)-C(9)	-0.3(3)
C(6)-N(3)-C(5)-C(4)	0.9(3)
C(6)-N(3)-C(5)-C(20)	177.6(2)
C(5)-N(3)-C(6)-C(7)	-2.1(3)
C(5)-N(3)-C(6)-C(11)	177.1(2)
N(1)-C(7)-C(6)-N(3)	0.4(3)
C(8)-C(7)-C(6)-N(3)	178.7(2)
N(1)-C(7)-C(6)-C(11)	-178.9(2)
C(8)-C(7)-C(6)-C(11)	-0.6(3)
C(26)-C(27)-C(28)-C(29)	1.3(3)
C(30)-C(29)-C(28)-C(27)	-0.7(4)
C(28)-C(27)-C(26)-C(31)	-0.5(3)
C(28)-C(27)-C(26)-C(12)	176.9(2)
C(30)-C(31)-C(26)-C(27)	-0.8(3)
C(30)-C(31)-C(26)-C(12)	-178.3(2)
C(7)-N(1)-C(4)-C(5)	-4.0(3)
Re(1)-N(1)-C(4)-C(5)	168.02(16)
C(7)-N(1)-C(4)-C(14)	176.2(2)
Re(1)-N(1)-C(4)-C(14)	-11.8(3)
N(3)-C(5)-C(4)-N(1)	2.3(3)
C(20)-C(5)-C(4)-N(1)	-174.3(2)
N(3)-C(5)-C(4)-C(14)	-177.9(2)
C(20)-C(5)-C(4)-C(14)	5.5(3)

C(15)-C(14)-C(4)-N(1)	-69.9(3)
C(19)-C(14)-C(4)-N(1)	114.5(3)
C(15)-C(14)-C(4)-C(5)	110.3(3)
C(19)-C(14)-C(4)-C(5)	-65.3(3)
C(28)-C(29)-C(30)-C(31)	-0.7(4)
C(26)-C(31)-C(30)-C(29)	1.4(4)
C(24)-C(25)-C(20)-C(21)	3.4(4)
C(24)-C(25)-C(20)-C(5)	-175.7(2)
N(3)-C(5)-C(20)-C(21)	133.9(2)
C(4)-C(5)-C(20)-C(21)	-49.3(3)
N(3)-C(5)-C(20)-C(25)	-47.0(3)
C(4)-C(5)-C(20)-C(25)	129.7(2)
C(19)-C(14)-C(15)-C(16)	-0.1(3)
C(4)-C(14)-C(15)-C(16)	-175.7(2)
N(3)-C(6)-C(11)-C(10)	-178.9(2)
C(7)-C(6)-C(11)-C(10)	0.3(3)
C(6)-C(11)-C(10)-C(9)	0.8(4)
C(13)-N(4)-C(9)-C(8)	1.3(3)
C(13)-N(4)-C(9)-C(10)	-176.8(2)
N(2)-C(8)-C(9)-N(4)	2.8(3)
C(7)-C(8)-C(9)-N(4)	-176.6(2)
N(2)-C(8)-C(9)-C(10)	-179.2(2)
C(7)-C(8)-C(9)-C(10)	1.5(3)
C(11)-C(10)-C(9)-N(4)	176.3(2)
C(11)-C(10)-C(9)-C(8)	-1.7(4)
C(25)-C(20)-C(21)-C(22)	-2.6(4)
C(5)-C(20)-C(21)-C(22)	176.5(2)
C(15)-C(14)-C(19)-C(18)	0.8(3)
C(4)-C(14)-C(19)-C(18)	176.4(2)
C(34)-C(33)-C(32)-C(37)	0.1(4)
C(34)-C(33)-C(32)-C(13)	177.4(2)
C(20)-C(25)-C(24)-C(23)	-1.0(4)
C(33)-C(32)-C(37)-C(36)	-2.3(4)
C(13)-C(32)-C(37)-C(36)	-179.6(2)
C(32)-C(37)-C(36)-C(35)	2.7(4)
C(14)-C(19)-C(18)-C(17)	-1.0(4)

C(37)-C(36)-C(35)-C(34)	-1.0(4)
C(19)-C(18)-C(17)-C(16)	0.4(4)
C(20)-C(21)-C(22)-C(23)	-0.6(4)
C(36)-C(35)-C(34)-C(33)	-1.3(4)
C(32)-C(33)-C(34)-C(35)	1.7(4)
C(18)-C(17)-C(16)-C(15)	0.4(4)
C(14)-C(15)-C(16)-C(17)	-0.5(4)
O(7)-Re(2)-O(4)-Re(1)	-38.6(2)
O(6)-Re(2)-O(4)-Re(1)	-159.14(18)
O(5)-Re(2)-O(4)-Re(1)	81.42(19)
C(21)-C(22)-C(23)-C(24)	3.0(4)
C(25)-C(24)-C(23)-C(22)	-2.1(4)
C(8)-N(2)-C(12)-C(13)	-0.2(3)
Re(1)-N(2)-C(12)-C(13)	-173.76(16)
C(8)-N(2)-C(12)-C(26)	178.66(19)
Re(1)-N(2)-C(12)-C(26)	5.1(3)
C(27)-C(26)-C(12)-N(2)	74.1(3)
C(31)-C(26)-C(12)-N(2)	-108.4(3)
C(27)-C(26)-C(12)-C(13)	-107.1(3)
C(31)-C(26)-C(12)-C(13)	70.4(3)
C(9)-N(4)-C(13)-C(12)	-4.8(3)
C(9)-N(4)-C(13)-C(32)	175.6(2)
N(2)-C(12)-C(13)-N(4)	4.4(4)
C(26)-C(12)-C(13)-N(4)	-174.5(2)
N(2)-C(12)-C(13)-C(32)	-176.0(2)
C(26)-C(12)-C(13)-C(32)	5.2(3)
C(37)-C(32)-C(13)-N(4)	57.0(3)
C(33)-C(32)-C(13)-N(4)	-120.3(3)
C(37)-C(32)-C(13)-C(12)	-122.7(3)
C(33)-C(32)-C(13)-C(12)	60.0(3)
Re(1)-O(4)-Re(2A)-O(6)	-152.5(6)
Re(1)-O(4)-Re(2A)-O(5)	26.6(18)
Re(1)-O(4)-Re(2A)-O(7)	-56.9(13)

Table S2. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	C14 H6 N2 O8 Re2	
Formula weight	702.61	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 14.1536(2) Å	α= 90°
	b = 14.5187(3) Å	β= 90°
	c = 15.7597(3) Å	γ = 90°
Volume	3238.49(10) $Å^3$	
Z	8	
Density (calculated)	2.882 Mg/m^3	
Absorption coefficient	29.258 mm^{-1}	
F(000)	2544	
Crystal size	0.110 x 0.040 x 0.010 mm^3	
Theta range for data collection	5.189 to 73.097°	
Index ranges	-17<=h<=13, -17<=k<=18, -19<=l<=18	
Reflections collected	17195	
Independent reflections	3230 [R(int) = 0.0575]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.77628	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3230 / 0 / 235	
Goodness-of-fit on F^2	1.135	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0844	
R indices (all data)	R1 = 0.0353, wR2 = 0.0860	
Largest diff. peak and hole	1.734 and -1.093 e. $Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **2**.

C(1)-O(1)	1.136(9)
C(1)-Re(1)	1.907(8)
C(2)-O(2)	1.127(10)
C(2)-Re(1)	1.916(7)
C(3)-O(3)	1.149(10)
C(3)-Re(1)	1.930(8)
C(4)-N(1)	1.338(11)
C(4)-C(5)	1.390(13)
C(4)-H(4)	0.9300
C(5)-C(6)	1.380(16)
C(5)-H(5)	0.9300
C(6)-C(7)	1.372(14)
C(6)-H(6)	0.9300
C(7)-C(8)	1.383(10)
C(7)-C(14)	1.511(13)
C(8)-N(1)	1.345(10)
C(8)-C(9)	1.438(11)
C(9)-N(2)	1.324(9)
C(9)-C(10)	1.389(10)
C(10)-C(11)	1.360(12)
C(10)-C(14)	1.533(11)
C(11)-C(12)	1.391(12)
C(11)-H(11)	0.9300
C(12)-C(13)	1.389(11)
C(12)-H(12)	0.9300
C(13)-N(2)	1.362(10)
C(13)-H(13)	0.9300
C(14)-O(4)	1.208(10)
N(1)-Re(1)	2.223(6)
N(2)-Re(1)	2.227(6)
O(5)-Re(2)	1.718(6)
O(5)-Re(1)	2.171(6)
O(6)-Re(2)	1.712(6)
O(7)-Re(2)	1.709(6)

O(8)-Re(2)	1.718(6)
O(1)-C(1)-Re(1)	175.2(6)
O(2)-C(2)-Re(1)	178.2(7)
O(3)-C(3)-Re(1)	175.0(7)
N(1)-C(4)-C(5)	121.4(9)
N(1)-C(4)-H(4)	119.3
C(5)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	122.2(8)
C(6)-C(5)-H(5)	118.9
C(4)-C(5)-H(5)	118.9
C(7)-C(6)-C(5)	117.6(8)
C(7)-C(6)-H(6)	121.2
C(5)-C(6)-H(6)	121.2
C(6)-C(7)-C(8)	116.2(9)
C(6)-C(7)-C(14)	137.2(8)
C(8)-C(7)-C(14)	106.5(7)
N(1)-C(8)-C(7)	127.9(8)
N(1)-C(8)-C(9)	121.7(7)
C(7)-C(8)-C(9)	110.4(7)
N(2)-C(9)-C(10)	127.8(7)
N(2)-C(9)-C(8)	120.3(7)
C(10)-C(9)-C(8)	111.8(7)
C(11)-C(10)-C(9)	117.8(7)
C(11)-C(10)-C(14)	137.3(7)
C(9)-C(10)-C(14)	104.9(7)
C(10)-C(11)-C(12)	117.0(7)
C(10)-C(11)-H(11)	121.5
C(12)-C(11)-H(11)	121.5
C(13)-C(12)-C(11)	121.2(7)
C(13)-C(12)-H(12)	119.4
C(11)-C(12)-H(12)	119.4
N(2)-C(13)-C(12)	122.4(7)
N(2)-C(13)-H(13)	118.8
C(12)-C(13)-H(13)	118.8
O(4)-C(14)-C(7)	127.2(8)
O(4)-C(14)-C(10)	126.5(9)

C(7)-C(14)-C(10)	106.3(6)
C(4)-N(1)-C(8)	114.7(7)
C(4)-N(1)-Re(1)	136.5(6)
C(8)-N(1)-Re(1)	108.8(5)
C(9)-N(2)-C(13)	113.7(6)
C(9)-N(2)-Re(1)	109.9(5)
C(13)-N(2)-Re(1)	136.0(5)
Re(2)-O(5)-Re(1)	162.3(3)
C(1)-Re(1)-C(2)	85.7(3)
C(1)-Re(1)-C(3)	88.5(3)
C(2)-Re(1)-C(3)	91.0(3)
C(1)-Re(1)-O(5)	175.0(3)
C(2)-Re(1)-O(5)	93.2(3)
C(3)-Re(1)-O(5)	96.4(3)
C(1)-Re(1)-N(1)	93.5(3)
C(2)-Re(1)-N(1)	97.6(3)
C(3)-Re(1)-N(1)	171.4(3)
O(5)-Re(1)-N(1)	81.8(2)
C(1)-Re(1)-N(2)	99.3(2)
C(2)-Re(1)-N(2)	173.8(3)
C(3)-Re(1)-N(2)	93.0(3)
O(5)-Re(1)-N(2)	81.5(2)
N(1)-Re(1)-N(2)	78.4(2)
O(7)-Re(2)-O(6)	108.6(3)
O(7)-Re(2)-O(5)	108.8(3)
O(6)-Re(2)-O(5)	110.6(3)
O(7)-Re(2)-O(8)	108.1(3)
O(6)-Re(2)-O(8)	110.1(3)
O(5)-Re(2)-O(8)	110.6(3)

Table 3. Torsion angles [°] for **2**.

N(1)-C(4)-C(5)-C(6)	-1.8(14)
C(4)-C(5)-C(6)-C(7)	2.1(14)
C(5)-C(6)-C(7)-C(8)	-0.4(12)
C(5)-C(6)-C(7)-C(14)	178.9(9)
C(6)-C(7)-C(8)-N(1)	-1.9(12)
C(14)-C(7)-C(8)-N(1)	178.6(7)
C(6)-C(7)-C(8)-C(9)	175.6(7)
C(14)-C(7)-C(8)-C(9)	-4.0(8)
N(1)-C(8)-C(9)-N(2)	3.3(10)
C(7)-C(8)-C(9)-N(2)	-174.4(6)
N(1)-C(8)-C(9)-C(10)	-179.8(6)
C(7)-C(8)-C(9)-C(10)	2.6(8)
N(2)-C(9)-C(10)-C(11)	-1.9(11)
C(8)-C(9)-C(10)-C(11)	-178.5(7)
N(2)-C(9)-C(10)-C(14)	176.7(7)
C(8)-C(9)-C(10)-C(14)	0.1(8)
C(9)-C(10)-C(11)-C(12)	1.5(11)
C(14)-C(10)-C(11)-C(12)	-176.4(8)
C(10)-C(11)-C(12)-C(13)	-0.2(12)
C(11)-C(12)-C(13)-N(2)	-1.3(13)
C(6)-C(7)-C(14)-O(4)	3.8(16)
C(8)-C(7)-C(14)-O(4)	-176.8(8)
C(6)-C(7)-C(14)-C(10)	-175.5(10)
C(8)-C(7)-C(14)-C(10)	3.9(8)
C(11)-C(10)-C(14)-O(4)	-3.5(15)
C(9)-C(10)-C(14)-O(4)	178.4(8)
C(11)-C(10)-C(14)-C(7)	175.7(9)
C(9)-C(10)-C(14)-C(7)	-2.4(8)
C(5)-C(4)-N(1)-C(8)	-0.4(12)
C(5)-C(4)-N(1)-Re(1)	-179.4(6)
C(7)-C(8)-N(1)-C(4)	2.2(11)
C(9)-C(8)-N(1)-C(4)	-174.9(7)
C(7)-C(8)-N(1)-Re(1)	-178.4(6)
C(9)-C(8)-N(1)-Re(1)	4.4(8)

C(10)-C(9)-N(2)-C(13)	0.5(10)
C(8)-C(9)-N(2)-C(13)	176.9(6)
C(10)-C(9)-N(2)-Re(1)	174.8(6)
C(8)-C(9)-N(2)-Re(1)	-8.9(8)
C(12)-C(13)-N(2)-C(9)	1.1(10)
C(12)-C(13)-N(2)-Re(1)	-171.1(6)
Re(1)-O(5)-Re(2)-O(7)	-90.4(12)
Re(1)-O(5)-Re(2)-O(6)	150.4(11)
Re(1)-O(5)-Re(2)-O(8)	28.1(12)

References

[1] J. Nasielski, R. Nasielski-Hinkens, S. Heilporn, C. Rypens, J.P. Declercq, Bull. Soc. Chim. Belg. 97 (1988) 983.

[2] M. Frisch, et al., GAUSSIAN09. 2009. Gaussian Inc., Wallingford, CT, USA. http://www.gaussian.com

[3] D. Andrae, U. Häußermann, M. Dolg, H. Stoll & H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.

[4] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, & T. L. Windus, *J. Chem. Info. & Model*., 2007, **47**, 1045–1052.

[5] R. C. Clark, and J. S. Reid, *Acta Cryst*. 1995, A**64**, 887–897.

[6] SuperNova Eos S2 System: Empirical absorption correction, 2011, *CrysAlis*-Software package, Oxford Diffraction Ltd.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, H., *J. Appl. Cryst*., 2009, **42**, 339–341 and Agilent (2012). *AutoChem* 2.0, in conjunction with *OLEX2*. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.

[8] G. M. Sheldrick, *Acta Cryst*., 2008, A**64**, 112–122.

[9] A. L. Spek, *Acta Cryst*., 2009, D**65**, 148–155.