Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Novel Re(I) dendrimers: synthesis, characterization and theoretical studies

Zhenjun Si [a, b], Xiaona Li[a], Xiyan Li[a], Guohai Xu[a], Zhiyong Guo[a], Hongjie Zhang[*,a], and Liang Zhou[a]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China. Fax: +86 43185698041; Tel: 86 431 85262127; E-mail: hongjie@ciac.jl.cn (H.-J. Zhang)
[b] School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, People's Republic of China. Fax: +86 43185583015; Tel: +86 43185583016; E-mail: sizj168@126.com (Zhenjun Si)

Table S1. Selected bond lengths (Å) and angles (deg) for **P1** and **P2.**

	P1		**P2**	
	Experimental	Theoretical	Experimental	Theoretical
C(1)-Re(1)	1.881(7)	1.914	1.981(8)	1.914
C(2)-Re(1)	1.909(6)	1.925	1.921(7)	1.925
C(3)-Re(1)	1.927(7)	1.925	1.933(8)	1.925
N(1)-Re(1)	2.182(4)	2.186	2.161(5)	2.186
N(2)-Re(1)	2.175(5)	2.186	2.177(5)	2.186
Br(1)-Re(1)	2.6246(7)	2.677	2.6285(7)	2.677
O(1)-C(1)-Re(1)	176.9(5)	179.7	174.4(7)	179.8
O(2)-C(2)-Re(1)	178.3(6)	177.2	178.6(6)	177.2
O(3)-C(3)-Re(1)	177.2(6)	177.3	175.5(6)	177.3
C(13)-N(2)-Re(1)	126.3(4)	125.8	126.7(4)	125.8
C(12)-N(2)-Re(1)	114.8(4)	115.2	115.2(4)	115.2
C(5)-N(1)-Re(1)	125.7(4)	125.4	126.6(4)	125.4
C(4)-N(1)-Re(1)	115.8(4)	115.3	115.3(4)	115.3
C(1)-Re(1)-C(2)	89.8(3)	92.1	88.4(3)	92.2
C(1)-Re(1)-C(3)	88.9(3)	92.2	90.4(3)	92.1
C(2)-Re(1)-C(3)	87.5(3)	90.7	89.8(3)	90.7
C(1)-Re(1)-N(1)	94.5(2)	93.5	90.2(2)	93.4
C(2)-Re(1)-N(1)	98.5(2)	96.6	98.6(2)	96.5
C(3)-Re(1)-N(1)	173.1(2)	170.6	171.5(2)	170.7
C(1)-Re(1)-N(2)	95.6(2)	93.4	96.9(2)	93.4
C(2)-Re(1)-N(2)	172.3(2)	170.7	172.2(2)	170.6
C(3)-Re(1)-N(2)	98.1(2)	96.6	95.8(2)	96.6
N(1)-Re(1)-N(2)	75.64(17)	75.62	75.75(19)	75.62
C(1)-Re(1)-Br(1)	178.5(2)	177.0	169.94(18)	177.02
C(2)-Re(1)-Br(1)	89.8(2)	89.8	87.6(2)	89.9
C(3)-Re(1)-Br(1)	92.51(18)	90.1	98.8(2)	90.0
N(1)-Re(1)-Br(1)	84.15(13)	83.93	81.28(13)	84.19
N(2)-Re(1)-Br(1)	84.59(12)	84.34	86.25(13)	84.27

Table S2. Frontier molecular orbital compositions (%) in the ground state for P1 and **P2 at B3LYP/LANL2DZ level**

Orbital	P1						P2					
	E (eV)	Bond type	Contribution (%)				E (eV)	Bond type	Contribution (%)			
			Re	CO	Br	**L1**			Re	CO	Br	**L2**
LUMO+3	-1.06	π*(L)				72.3L′ 22.5R1	-1.03	π*(L)				93.3L′
LUMO+2	-2.01	π*(L)				93.1L′	-1.96	π*(L)				97.8L′
LUMO+1	-2.52	π*(L)				97.5L′	-2.49	π*(L)				98.9L′
LUMO	-2.78	π*(L)				90.4L′	-2.76	π*(L)				90.4L′
HOMO-LUMO gap	2.73						2.73					
HOMO	-5.51	d(Re) π(CO) π(Br)	11.4 d_{z^2} 5.1 d_{yz} 3.4 $d_{x^2-y^2}$	14.4	57.2		-5.49	d(Re) π(CO) π(Br)	16.9 d_{z^2} 1.1 d_{yz} 4.4 $d_{x^2-y^2}$	14.4	57.2	
HOMO-1	-5.55	d(Re) π(CO) π(Br)	13.9 d_{xz} 3.6 d_{xy}	11.1	59.6		-5.53	d(Re) π(CO) π(Br)	8.8 d_{xz} 5.5 d_{xy}	10.8	58.0	
HOMO-2	-5.78	π(L)				19.8L′ 79.5 R1	-5.59	π(L)				65.4L′ 30.7R2
HOMO-3	-6.19	π(L)				99.5R1	-6.01	π(L)				96.6L′

Table S3. Frontier molecular orbital compositions (%) in the ground state for D1 and **D2 at B3LYP/LANL2DZ level**

Orbital	D1						D2					
	E (eV)	Bond type	Contribution (%)				E (eV)	Bond type	Contribution (%)			
			Re	CO	Br	**L3**			Re	CO	Br	**L4**
LUMO+3	-1.49	π*(L)				97.6R3	-1.42	π*(L)				97.6R4
LUMO+2	-2.15	π*(L)				92.5L′	-2.13	π*(L)				92.6L′
LUMO+1	-2.623	π*(L)				96.8L′	-2.61	π*(L)				96.9L′
LUMO	-2.87	π*(L)				90.4L′	-2.85	π*(L)				90.4L′
HOMO-LUMO gap	2.55						2.38					
HOMO	-5.42	π(L)				97.2R3	-5.23	π(L)				97.7R4
HOMO-1	-5.54	π(L)				99.8R3	-5.34	π(L)				99.8R4
HOMO-2	-5.58	d(Re) π(CO) π(Br)	$13.7\,d_{z^2}$ $4.7\,d_{x^2-y^2}$	14.9	55.9		-5.56	d(Re) π(CO) π(Br)	$16.2\,d_{z^2}$ $4.8\,d_{x^2-y^2}$	14.9	55.9	
HOMO-3	-5.62	d(Re) π(CO) π(Br)	$8.9\,d_{xz}$ $6.6\,d_{xy}$	11.5	58.6		-5.60	d(Re) π(CO) π(Br)	$6.3\,d_{xz}$ $11.6\,d_{xy}$	11.5	58.6	

Table S4. Selected triplet-absorption parameters of P1, P2, D1, and D2 in CH_2Cl_2 according to TDDFT (LANL2DZ) calculations

Complex	State	Transition	λ(nm) / E(eV)	Assignment
P1	T_1	H→L	507/2.44	d→π*/π→π*
	T_2	H-1→L	501/2.47	d→π*/π→π*
	T_3	H-1→L	485/2.56	d→π*/π→π*
	T_4	H-2→L	476/2.60	π→π*
	T_5	H→L+2	430/2.88	d→π*/π→π*
P2	T_1	H→L	521/2,38	d→π*/π→π*
	T_2	H-2→L	504/2.46	π→π*
	T_3	H-2→L	489/2.54	π→π*
	T_4	H-1→L	483/2.57	d→π*/π→π*
	T_5	H→L+2	435/2.85	d→π*/π→π*
D1	T_1	H→L	517/2.40	π→π*
	T_2	H-4→L	502/2.47	π→π*
	T_3	H-5→L	493/2.51	π→π*
	T_4	H→L+1	480/2.58	π→π*
	T_5	H-1→L	473/2.62	π→π*
D2	T_1	H→L	543/2.28	π→π*
	T_2	H-1→L	504/2.46	π→π*
	T_3	H-5→L	503/2.46	π→π*
	T_4	H-6→L	496/2.50	π→π*
	T_5	H→L+1	489/2.54	π→π*

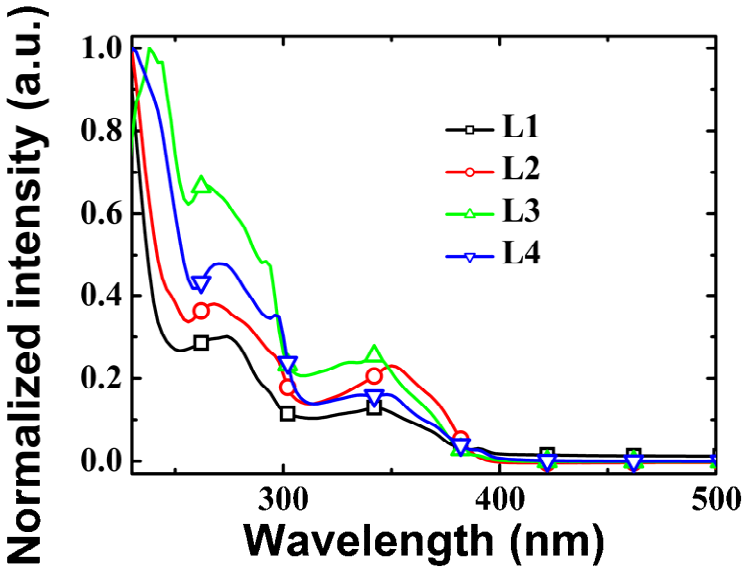


Fig. S1. Absorption spectra of **L1 – L4** in CH_2Cl_2.

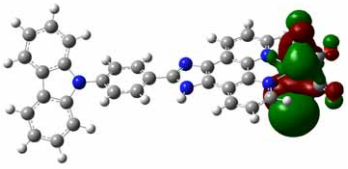
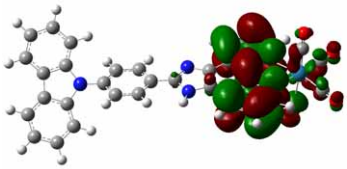
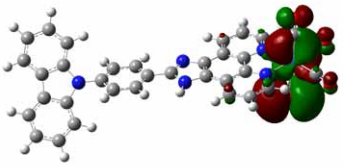
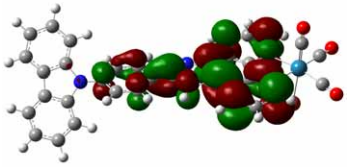
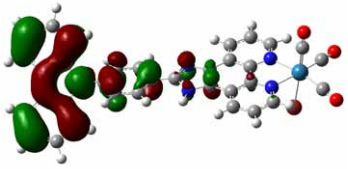
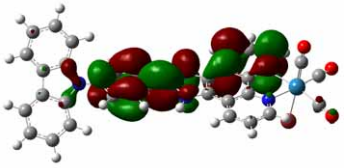
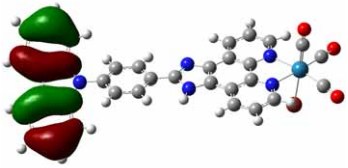
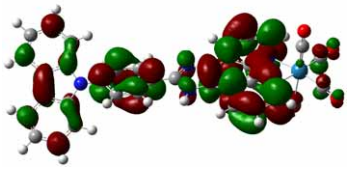
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2		LUMO+2	
HOMO-3		LUMO+3	

Fig. S2. Electron density plots of the frontier orbitals for **P1**.

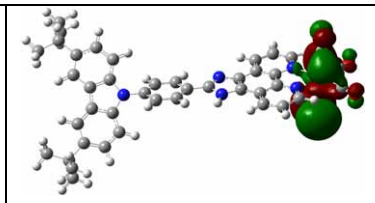
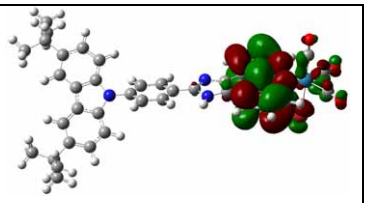
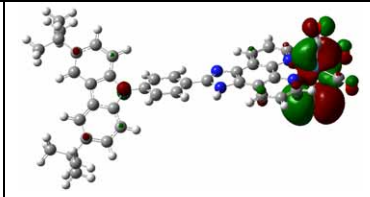
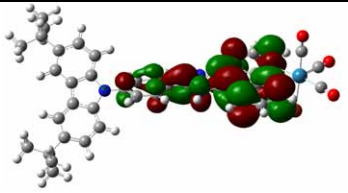
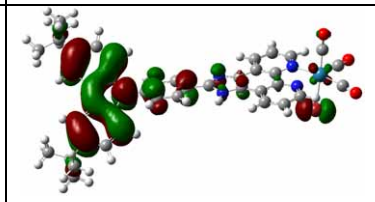
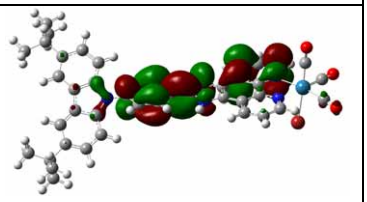
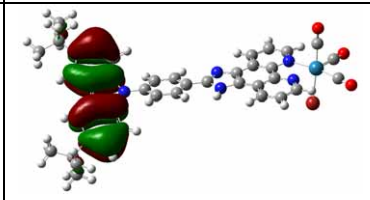
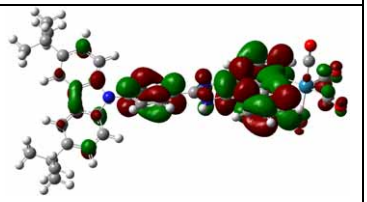
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2		LUMO+2	
HOMO-3		LUMO+3	

Fig. S3. Electron density plots of the frontier orbitals for **P2**.

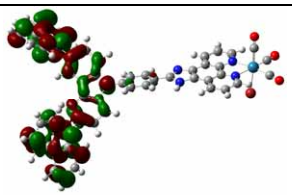
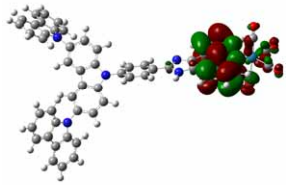
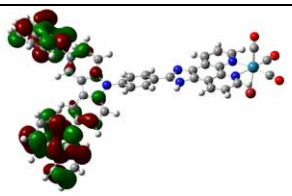
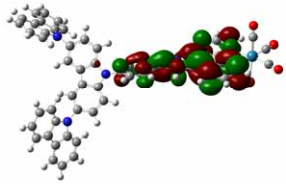
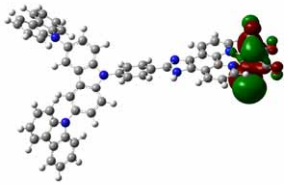
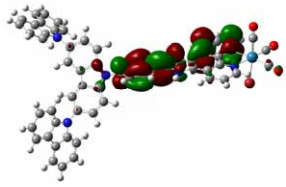
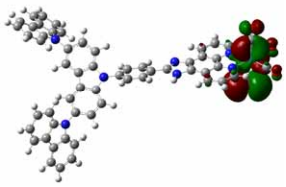
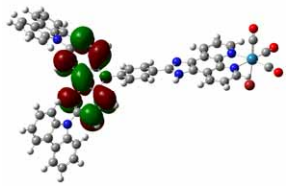
HOMO			LUMO	
HOMO-1			LUMO+1	
HOMO-2			LUMO+2	
HOMO-3			LUMO+3	

Fig. S4. Electron density plots of the frontier orbitals for **D1**.

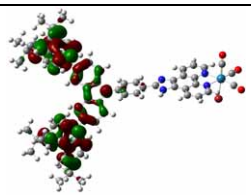
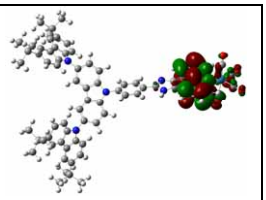
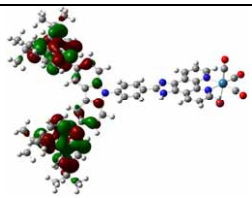
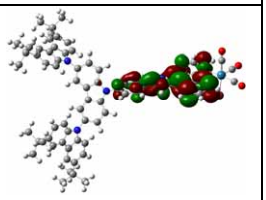
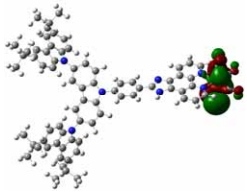
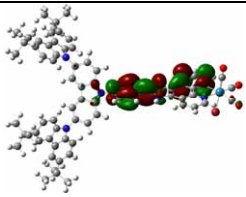
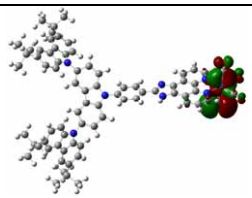
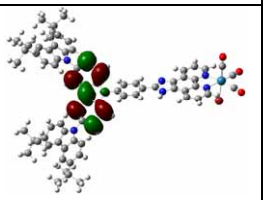
HOMO			LUMO	
HOMO-1			LUMO+1	
HOMO-2			LUMO+2	
HOMO-3			LUMO+3	

Fig. S5. Electron density plots of the frontier orbitals for **D2**.