Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Sandwich-type Tetrakis(phthalocyaninato) Rare Earth(III)-Cadimium(II) Quadruple-deckers. The Effect of f-Electrons

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Caption of Content

Figure S1. Yield of the quadruple-decker compounds **1-12** as a function of the rare earth ionic radius M^{III}.

Figure S2. IR spectra of {[Pc(OC_8H_{17})$_8$]Eu[Pc(OC_8H_{17})$_8$]Cd[Pc(OC_8H_{17})$_8$]Eu[Pc(OC_8H_{17})$_8$]} (**5**) in the region of 400-4000 cm^{-1} with 2 cm^{-1} resolution.

Figure S3. Cyclic voltammetry of {[Pc(OC_8H_{17})$_8$]Tb-[Pc(OC_8H_{17})$_8$]Cd-[Pc(OC_8H_{17})$_8$]Tb[Pc(OC_8H_{17})$_8$]} (7) in CH_2Cl_2 containing 0.1 M [NBu_4][ClO_4] at scan rate of 40 mV/s.

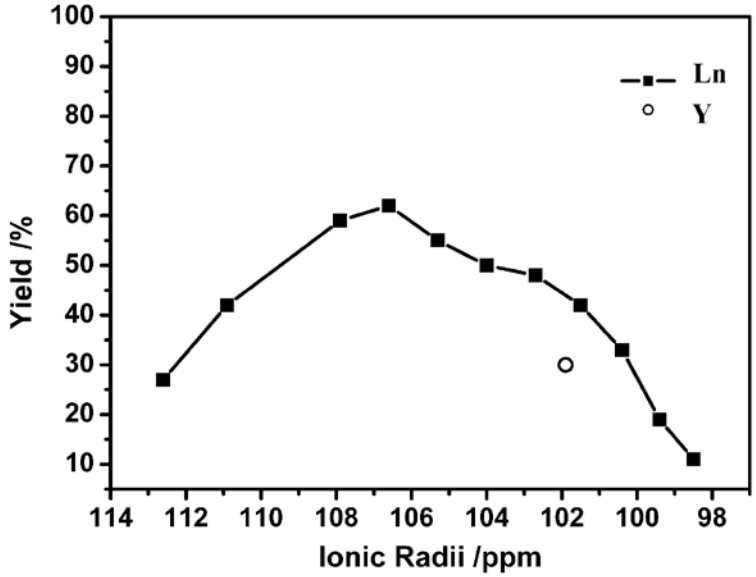
Table S1. Mass spectroscopic and elemental analysis data for the compounds **1-12**.

Table S2. ^{1}H NMR data (δ) and corresponding assignments for the compounds **1-12** in $CDCl_3$.

Table S3. Electronic absorption data for the compounds **1-12** in toluene.

Table S4. Half-wave redox potentials of the compounds **1-12**(V vs SCE) in CH_2Cl_2 containing 0.1 M TBAP.

Table S5. The effective imaginary third order molecular hyperpolarizability Im{$\chi^{(3)}$} value of the compounds **1-12** in toluene solution under an open-aperture configuration.



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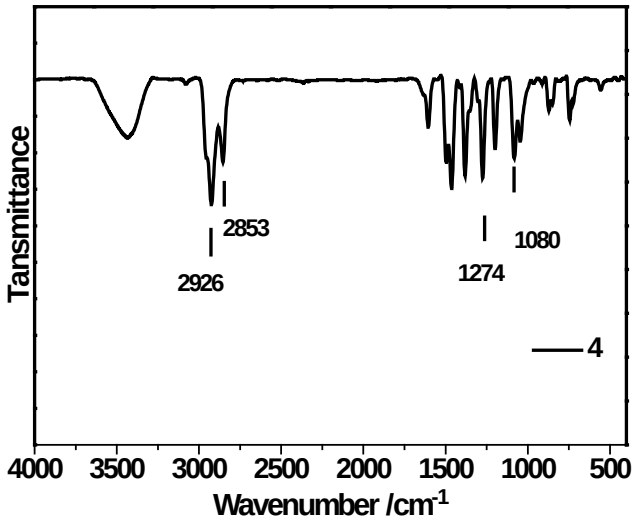

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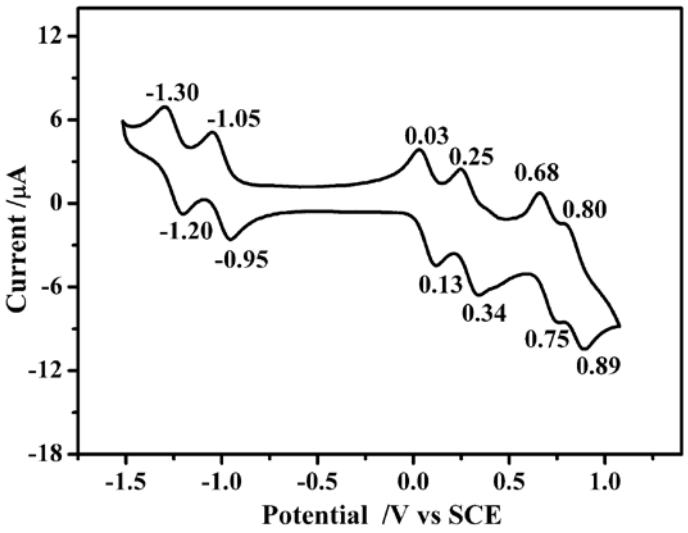

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Table S1. Mass spectroscopic and elemental analysis data for the compounds **1-12**.[a]

Compound	Yield (%)	M^+ (*m/z*)[b]	Analysis (%)[a,b]		
			C	H	N
$C_{384}H_{576}CdN_{32}O_{32}Y_2$ (**1**)[c]	30	6441.5 (6441.2)	70.46 (71.58)	8.86 (9.01)	6.83 (6.96)
$C_{384}H_{576}CdN_{32}O_{32}Pr_2$ (**2**)[d]	27	6545.3 (6545.2)	70.25 (70.45)	8.87 (8.87)	6.83 (6.85)
$C_{384}H_{576}CdN_{32}O_{32}Nd_2$ (**3**)[c]	42	6547.1 (6547.2)	69.29 (70.37)	8.72 (8.86)	6.72 (6.84)
$C_{384}H_{576}CdN_{32}O_{32}Sm_2$ (**4**)	59	6567.9 (6567.2)	70.24 (70.24)	8.84 (8.84)	6.83 (6.83)
$C_{384}H_{576}CdN_{32}O_{32}Eu_2$ (**5**)[c]	62	6569.0 (6569.2)	69.13 (70.21)	8.70 (8.82)	6.70 (6.82)
$C_{384}H_{576}CdN_{32}O_{32}Gd_2$ (**6**)[d]	55	6578.9 (6579.2)	69.90 (70.10)	8.83 (8.82)	6.79 (6.81)
$C_{384}H_{576}CdN_{32}O_{32}Tb_2$ (**7**)[d]	50	6581.4 (6581.2)	69.87 (70.06)	8.83 (8.82)	6.79 (6.81)
$C_{384}H_{576}CdN_{32}O_{32}Dy_2$ (**8**)	48	6590.7 (6591.2)	69.68 (69.98)	8.85 (8.81)	6.70 (6.80)
$C_{384}H_{576}CdN_{32}O_{32}Ho_2$ (**9**)[c]	42	6593.6 (6593.2)	68.87 (69.93)	8.67 (8.80)	6.68 (6.80)
$C_{384}H_{576}CdN_{32}O_{32}Er_2$ (**10**)[e]	33	6595.1 (6595.2)	69.50 (69.88)	8.41 (8.80)	6.85 (6.79)
$C_{384}H_{576}CdN_{32}O_{32}Tm_2$ (**11**)[e]	19	6600.9 (6601.2)	69.47 (69.85)	8.81 (8.79)	6.75 (6.79)
$C_{384}H_{576}CdN_{32}O_{32}Yb_2$ (**12**)[d]	11	6611.0 (6611.2)	69.57 (69.76)	8.79 (8.78)	6.76 (6.78)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion M^+. [c] Contain 1.0 equiv. of solvated $CHCl_3$.[d] Contain 1.0 equiv. of solvated H_2O. [e] Contain 2.0 equiv. of solvated H_2O.

Table S2. ^{1}H NMR data (δ) and assignments of the quandruple complexes in $CDCl_3$.

Complex	location	**H**$^{\alpha}$	-O**CH$_2$**-	-OCH$_2$**(CH$_2$)$_6$**-	-OCH$_2$(CH$_2$)$_6$**CH$_3$**
1	outer	9.47 (s, 16H)	3.33 (m, 32H)		0.87 (t, 48H)
	inner	10.12 (s, 16H)	4.88 (m, 16H) 3.92 (m, 16H)	2.69-1.23 (m, 384H)	0.87 (t, 48H)
2	outer	4.39 (s, 16H)	2.81 (m, 16H) 2.62 (m, 16H)		0.75 (t, 48H)
	inner	5.49 (s, 16H)	3.48 (m, 16H) 3.20 (m, 16H)	1.51-0.93 (m, 384H)	0.83 (t, 48H)
3	outer	6.79 (s, 16H)	3.97 (m, 32H)	1.87 (m, 32H) 1.85 (m, 32H) 1.49 (m, 64H) 1.33 (m, 64H)	0.91 (t, 48H)
	inner	7.12 (s, 16H)	4.15 (m, 32H)	2.17 (m, 32H) 1.85 (m, 32H) 1.61 (m, 64H) 1.38 (m, 64H)	1.03 (t, 48H)
4	outer	8.78 (s, 16H)	5.09 (m, 16H) 4.48 (m, 16H)	2.38 (m, 32H) 2.02 (m, 32H) 1.89 (m, 64H) 1.49 (m, 64H)	0.97 (t, 48H)
	inner	9.37 (s, 16H)	5.68 (m, 32H)	3.24 (m, 32H) 2.82 (m, 32H) 2.38 (m, 32H) 2.30 (m, 32H) 2.02 (m, 32H) 1.62 (m, 32H)	1.32 (t, 48H)
5	Not observed				
6	outer	-50.39(s, 16H)	-31.33 (m,32H)	-14.78(m,64H) -13.49(m,32H) -12.16(m,32H) -9.88 (m, 32H) -4.83 (m, 32H)	-1.90 (t, 48H)
	inner	-52.04(s, 16H)	-33.78(m, 32H)	-22.07(m,32H) -18.90(m, 2H) -14.78(m,32H) -12.16(m,32H) -9.88 (m, 32H) -4.83 (m, 32H)	-2.88 (t, 48H)

7	outer	-23.18(s, 16H)	-14.74(m, 32H)	-12.42(m,32H)	-0.67 (t, 48H)
				-10.20(m,32H)	
				-6.61 (m, 32H)	
				-5.31 (m, 32H)	
				-4.12 (m, 32H)	
				-2.25 (m, 32H)	
	inner	-24.18(s, 16H)	-15.84(m, 32H)	-15.84(m,32H)	-1.59 (t, 48H)
				-10.20(m,32H)	
				-8.64 (m, 32H)	
				-6.61 (m, 32H)	
				-5.77 (m, 32H)	
				-2.25 (m, 32H)	
8	outer	-5.32 (s, 16H)	-4.12 (m, 32H)	-0.92 (m, 32H)	1.20 (t, 48H)
				-0.83 (m, 32H)	
				-0.09 (m, 32H)	
				0.32 (m, 32H)	
				0.58 (m, 64H)	
	inner	-6.02 (s, 16H)	-4.29 (m, 32H)	-2.62 (m, 32H)	0.78 (t, 48H)
				-2.10 (m, 32H)	
				-1.42 (m, 32H)	
				-0.92 (m, 32H)	
				-0.47 (m, 32H)	
				0.32 (m, 32H)	
9	outer	7.55 (s, 16H)	4.41 (m, 16H)	2.50-1.31 (m, 384H)	0.98 (t, 48H)
			4.08 (m, 16H)		
	inner	7.66 (s, 16H)	4.66 (m, 32H)		1.13 (t, 48H)
10	outer	8.17 (s, 16H)	5.88 (m, 32H)	5.77 (m, 64H)	1.42 (t, 48H)
				3.30 (m, 32H)	
				2.97 (m, 32H)	
				2.30 (m, 32H)	
				2.07 (m, 32H)	
	inner	12.59 (s, 16H)	11.35 (m, 32H)	-22.07(m,32H)	3.88 (t, 48H)
				-18.90(m,32H)	
				-14.78(m,32H)	
				-12.16(m,32H)	
				-9.88 (m, 32H)	
				-4.83 (m, 32H)	
11	outer	27.23 (s, 16H)	14.32 (m, 16H)	6.60 (m, 32H)	1.48 (t, 48H)
			9.09 (m, 16H)	5.77 (m, 32H)	
				4.98 (m, 32H)	

				3.79 (m, 32H)	
				3.13 (m, 32H)	
				2.54 (m, 32H)	
	inner	34.75 (s, 16H)	21.55 (m, 16H)	13.44 (m, 32H)	2.03 (t, 48H)
			21.18 (m, 16H)	12.25 (m, 32H)	
				9.10 (m, 32H)	
				8.02 (m, 32H)	
				6.60 (m, 32H)	
				5.09 (m, 32H)	
12	outer	10.14 (s, 16H)	5.63 (m, 16H)	2.52 (m, 64H)	0.99 (t, 48H)
			4.70 (m, 16H)	2.27 (m, 32H)	
				2.08 (m, 64H)	
				1.70 (m, 32H)	
	inner	10.72 (s, 16H)	6.66 (m, 16H)	3.79 (m, 32H)	1.44 (t, 48H)
			6.62 (m, 16H)	3.33 (m, 32H)	
				2.70 (m, 64H)	
				2.27 (m, 32H)	
				1.70 (m, 32H)	

Table S3. Electronic absorption data for the compounds **1-12** in toluene.

Compound	λ_{max}/nm (log ε)			
1	355 (5.55)	576 (4.66)	629 (5.60)	704 (4.85)
2	354 (5.58)	579 (4.88)	635 (5.55)	693 (4.82)
3	355 (5.48)	580 (4.64)	634 (5.64)	696 (4.79)
4	355 (5.51)	580 (4.61)	632 (5.63)	698 (4.81)
5	355 (5.48)	579 (4.65)	631 (5.58)	699 (4.81)
6	355 (5.47)	578 (4.56)	631 (5.58)	701 (4.76)
7	355 (5.53)	578 (4.63)	629 (5.65)	705 (4.81)
8	355 (5.46)	577 (4.53)	629 (5.58)	705 (4.75)
9	356 (5.49)	579 (4.59)	629 (5.59)	710 (4.77)
10	356 (5.46)	577 (4.55)	628 (5.57)	715 (4.75)
11	356 (5.54)	577 (4.65)	628 (5.63)	713 (4.82)
12	355 (5.51)	575 (4.62)	627 (5.59)	717 (4.81)

Table S4. Half-wave redox potentials of the compounds **1-12**(V vs SCE) in CH_2Cl_2 containing 0.1 M TBAP.

Compound	**Oxd_4**	**Oxd_3**	**Oxd_2**	**Oxd_1**	**Red_1**	**Red_2**	**$\Delta E^o_{1/2}$[a]**
1	+0.98	+0.82	+0.40	+0.19	-0.84	-1.18	1.03
2	+0.91	+0.73	+0.50	+0.20	-0.97	-1.25	1.17
3	+0.95	+0.76	+0.49	+0.22	-0.94	-1.24	1.16
4	+0.94	+0.79	+0.43	+0.19	-0.95	-1.22	1.14
5	+0.94	+0.80	+0.41	+0.18	-0.95	-1.21	1.13
6	+0.90	+0.75	+0.36	+0.16	-0.93	-1.22	1.09
7	+0.85	+0.72	+0.30	+0.08	-1.00	-1.25	1.07
8	+0.88	+0.74	+0.31	+0.08	-0.98	-1.23	1.06
9	+0.86	+0.72	+0.30	+0.08	-0.97	-1.22	1.05
10	+0.89	+0.75	+0.32	+0.07	-0.98	-1.24	1.05
11	+0.86	+0.73	+0.29	+0.04	-1.00	-1.25	1.04
12	+0.86	+0.76	+0.27	+0.04	-0.96	-1.24	1.00

[a] $\Delta E^o_{1/2}$ is the potential difference between the first oxidation and the first reduction processes, i.e. the HOMO-LUMO gap of the complexes: $\Delta E^o_{1/2} = Oxd_1 - Red_1$.

Table S5. The effective imaginary third order molecular hyperpolarizability Im{$\chi^{(3)}$} value of the compounds **1-12** in toluene solution under an open-aperture configuration.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Im{$\chi^{(3)}$}(×10^{-11} esu)	24.1	21.5	21.4	21.4	22.4	22.5
Compound	**7**	**8**	**9**	**10**	**11**	**12**
Im{$\chi^{(3)}$}(×10^{-11} esu)	22.7	22.6	20.4	20.6	20.6	21.3