Supplementary Material (ESI) for Chemical Society Reviews

Lanthanide Luminescence for Functional Materials and Bio-Sciences

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Electronic Supporting Information

Table S1 Selected photophysical properties of NIR emitting Nd^{III}, Er^{III}, and Yb^{III} molecular compounds at room temperature (10.2006–3.2009).[a]

Composition	Ln	State	λ_{exc} / nm	Q_{Ln}^{L} / %	λ_{exc} / nm	τ / µs	Q_{Ln}^{Ln} / %	Refs
[Ln(**1a**)$_3$]	Nd	solid			355	0.33		1
	Er	solid				0.98		1
	Yb	solid				3.5		1
[NEt_4][Ln(**1b**)$_4$]	Nd	thf			355	0.51	0.20	2
		H_2O				0.47	0.19	2
	Yb	thf			355	8.3	0.41	2
		H_2O				1.4	0.07	2
[Ln(**2a**)$_3$]·nH_2O	Nd (n = 0)	solid	350–400	0.14	355	0.39		3
	Er (n = 3)	solid		0.012		1.15		3
	Yb (n = 2.5)	solid		0.56		11.1		3
[Ln(**2b**)$_3$]·nH_2O	Nd (n = 8)	solid	350–400	0.23	355	0.69		3
	Yb (n = 1)	solid		0.60		10.5		3
[Ln(**2c**)$_3$]·CH_3OH	Nd	solid	350–400	0.40	355	1.57		3
[Ln(**2c**)$_3$]·nH_2O	Er (n = 0)	solid	350–400	0.033	355	4.05		3
	Yb (n = 3)	solid		1.40		20.6		3
[Ln(**3**)$_2$][NO_3]	Yb	CH_3CN	500	1.1				4
[Ln(**4a**)$_3$]	Nd	solid	508–527	0.15	355	0.87	0.32	5
[Ln(**4b**)$_3$]	Nd	solid	508–527	0.11	355	0.47	0.17	5
[Ln(**4c**)$_3$]	Nd	solid	508–527	0.10	355	0.51	0.19	5
[Ln(**4d**)$_3$]·$2H_2O$	Nd	solid	508–527	0.04	355	0.33	0.12	5
[Ln(**4e**)$_3$]	Nd	solid	508–527	0.33	355	1.26	0.47	5
[Ln(**4f**)$_3$]	Nd	solid	508–527	0.26	355	1.88	0.70	5
[Ln(**4g**)$_3$]	Nd	solid	508–527	0.13	355	1.22	0.45	5
[Ln(**4h**)$_3$(H_2O)$_n$]	Nd (n = 0)	solid	508–527	0.29	355	1.82	0.67	5
	Yb (n = 1)	solid	508–527	0.07	355	0.82	0.07	5
[Ln(**4i**)$_3$]·$2.5H_2O$	Nd	solid	470	0.08	355	0.35	0.13	6
[Ln(**4j**)$_3$]·H_2O	Nd	solid	470	0.15	355	1.10	0.40	6

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
[Ln(**4k**)$_3$]·3H_2O	Nd	solid	470	0.11	355	0.75	0.28	6
[Ln(**4l**)$_3$]·H_2O	Nd	solid	470	0.26	355	1.20	0.44	6
[Ln(**4m**)$_3$]·H_2O	Nd	solid	470	0.18	355	1.10	0.41	6
[Ln(**4n**)$_3$]·3H_2O	Nd	solid	470	0.34	355	1.00	0.37	6
[Ln(**4o**)$_3$]·H_2O	Nd	solid	470	0.23	355	0.61	0.23	6
[KLn$_2$(**5a**)$_3$](OTf)	Yb	solid	395	1.04	355	18.8		7
[KAlLn(**5b**)$_3$](OTf)	Yb	solid	395	1.17	355	22.6		7
[Ln(H_3**6a**)]	Nd	H_2O, pH 7.4	417	0.027	355	0.15		8
		D_2O		0.075		0.91		8
	Er	H_2O, pH 7.4				0.24		8
		D_2O		3.5×10^{-3}		2.55		8
	Yb	H_2O, pH 7.4		0.13		2.47		8
		D_2O		1.5		26.6		8
[Ln(**6b**)]	Nd	solid	363	0.10	363	0.49		9
	Er	solid	371	4.3×10^{-3}	371	1.17		9
	Yb	solid	370	0.60	370	7.13		9
[Ln(**6c**)]	Nd	H_2O (pH 7.4)	370	0.016	370	0.16		9
	Er	H_2O (pH 7.4)	370	$<2\times10^{-3}$	370			9
	Yb	H_2O (pH 7.4)	370	0.14	370	2.05		9
[Ln(**7a**)$_3$]	Er	solid			520	4.9		10
[Ln(**7b**)$_3$]	Er	solid			520	$300^{b,c}$		10
[Ln(**7b**)$_3$]	Er	nanorods			978	13 (11%), 336 (89%)	0.98	11
[$Er_{0.5}Yb_{0.5}$(**7b**)$_3$]	Er	nanorods			978	19 (2%), 748 (98%)	3.5	11
[Ln(**7c**)$_3$]	Er	solid			520	179^{b}		12
[Ln(**8**)$_3$]	Nd	solid			266	46		13
		CD_3CN				44		13
	Er	solid				316		13
		CD_3CN				741		13

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
	Yb	solid				582		13
[Ln(**8**)$_3$]	Yb	CD_3CN				1111		13
[Ln(H_2**10**)$_2$]$^-$	Pr	H_2O, pH 7.4			?	8×10^{-3}		14
	Ho	H_2O, pH 7.4				6.5×10^{-3}		14
[Ln(H_2**11**)$_2$]$^-$	Nd	H_2O, pH 7.4			326	–		15
[Ln(H_2**11**)$_2$]$^-$	Nd	D_2O, pD 7.4				0.48		15
		CH_3OH				0.23		15
		CD_3OD				0.98		15
[Ln(H_2**11**)$_2$]$^-$	Yb	H_2O, pH 7.4				0.39 (70%), 1.01 (30%)		15
		D_2O, pH 7.4				3.30 (71%), 12.7 (29%)		15
		CH_3OH				1.76		15
		CD_3OD				38.4		15
[Ln(H_3**12**)(H_2O)$_2$]	Yb	H_2O, pH 7.4			337	0.37		16
		D_2O, pD 7.4				8.06		16
[Ln_2(**13a**)$_6$(phen)$_2$]	Er	solid			975	17.7		17
	Yb	solid				58.9		17
[$Er_{1.4}Yb_{0.6}$(**13a**)$_6$(phen)$_2$]	Er	solid			975	19.3		17
	Yb	solid				26.7		17
[Ln(**13b**)$_3$(tpy)]	Nd	toluene			416	0.97	0.39	18
		ethanol				0.55	0.22	18
	Er	toluene				0.72	9×10^{-3}	18
		ethanol				0.38	5×10^{-3}	18
	Yb	toluene				1.58	0.079	18
		ethanol				1.70	0.085	18
[Ln(**13c**)$_3$(tpy)]	Nd	toluene				0.10	0.04	18
		ethanol				0.30	0.12	18
	Er	toluene				0.18	2×10^{-3}	18
		ethanol				–	–	18
	Yb	toluene				0.65	0.033	18

		ethanol				0.70	0.035	18

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
[Ln(**14a**)$_3$(tpy)]	Er	chlorobenzene			300	2.13	0.027	19
		solid			350	1.91		19
[Ln(**14b**)$_3$(tpy)]	Er	chlorobenzene			300	2.22	0.028	19
	Er	solid			350	1.71		19
[Ln(**14c**)$_3$(tpy)]	Er	chlorobenzene			300	1.97	0.025	19
	Er	solid			350	1.38		19
[Ln(**14d**)$_3$(tpy)]	Er	solid			350	1.12		19
[Ln(**15**)$_3$]	Yb	CH_3CN	315	0.7				20
[NBu_4]$_3$[Ln(**16**)$_3$]	Nd	CH_2Cl_2			360	1.2		21
	Yb	CH_2Cl_2				37		21
[Ln(**17**)]$^-$	Yb	H_2O, pH 7.0			?	3.0	0.15	22
[Ln(**18a**)(H_2O)$_2$]$^-$	Nd	H_2O, pH 7.0	266	9.7×10^{-3}	266	0.059		23
		D_2O, pD 7.0		0.055		0.310		23
[Ln(**18b**)(H_2O)$_2$]$^-$	Nd	H_2O, pH 7.0	250	7.5×10^{-3}	266	0.072		23
		D_2O, pD 7.0		0.040		0.314		23
[Ln(**19**)]	Nd	CH_3OH			337	0.203		24
		CD_3OD				0.576		24
	Er	CH_3OH				0.134		24
		CD_3OD				1.009		24
	Yb	CH_3OH				1.802		24
		CD_3OD				9.047		24
[Ln(**20a**)$_3$(phen)]	Nd	dmso	430	7.8×10^{-3}	355	1.2	0.29	25
		solid			355	0.71		25
	Er	dmso	430	-	355	1.9		25
		solid			355	1.4		25
	Yb	dmso	430	0.04	355	12	0.60	25
		solid	430(?)	0.2 [c]		8.6 [c]	0.43 [c]	25
[Ln(**21b**)$_3$(phen)]	Er	toluene	355	0.019				26

		solid			355	2.73		26

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
[Ln(**21b**)$_3$(phen)]	Yb	toluene	355	1.28				26
		solid			355	14.7		26
[Ln(**21b**)$_3$(bpy)]	Nd	toluene	355	0.072				26
		solid			355	1.27		26
	Er	toluene	355	0.014				26
		solid			355	2.27		26
	Yb	toluene	355	1.24				26
		solid			355	13.8		26
[Ln(**21b**)$_3$(H_2O)$_2$]	Nd	toluene	355	8.5×10^{-3}				26
		solid			355	0.15		26
	Yb	toluene	355	0.37				26
		solid			355	0.97		26
[Ln(**21d**)$_3$(OP(C_6F_5)$_3$)$_2$]	Yb	CCl_4			355	2.4	2.4×10^{-2}	27
[Ln(**21e**)$_3$(OP(C_6F_5)$_3$)$_2$]	Yb	CCl_4			355	16.8	0.17	27
DMSB[Ln(**21f**)$_4$]	Nd	CH_3CN			266	1.0		28
	Er	CH_3CN			266	3.2		28
	Yb	CH_3CN			266	46.4		28
[Ln(**22**)$_4$]$^-$	Nd	CH_3OH			354	0.37		29
		CD_3OD			354	1.33		29
		CH_3CN	383	0.45	354	1.85		29
		CD_3CN	383	0.53	354	2.68		29
	Er	CH_3CN	387	0.021	354			29
		CD_3CN	387	0.024	354			29
	Tm	CH_3CN	380	5.9×10^{-3}	354			29
		CD_3CN	380	6.6×10^{-3}				29
	Yb	CH_3OH			354	12.01		29
		CD_3OD			354	33.71		29
	Yb	CH_3CN	375	3.8	354	24.61		29

		CD_3CN	375	4.2	354	32.81		29

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
Cs_2[Ln(**23a**)$_5$]	Er	solid			520	20.2		30
Cs_2[Ln(**23a**)$_5$](Et_2O)$_n$	Er (n = 1)	solid			520	22.9		30
Cs_2[Ln(**23a**)$_5$](Et_2O)$_n$	Yb (n = 0.5)	solid			460	142 (92%), 351 (8%)		30
[Ln(**24a**)$_3$(phen)$_2$]	Yb	dmso-d_6	310	0.67	940		7.4	31
[Ln(**24a**)$_3$(dip)]	Yb	dmso-d_6	310	0.36	940		9.1	31
K[Ln(**24b**)$_4$]	Nd	dmso			354	1.10		32
$NaY_{0.8}Ln_{0.2}F_4$@**24b**	Nd	nanocrystal			354	3.7 (63%), 12.6 (22%)		33
K[Ln(**24b**)$_4$]	Yb	dmso			354	12.4		32
$NaY_{0.8}Ln_{0.2}F_4$@**24b**	Yb	nanocrystal			354	68 (80%), 4.1(20%)		33
[Ln(**25**)]	Nd	H_2O, pH 8.0			488	2.3		34
[Ln(**26**)]$^{3+}$	Nd	CH_3OH			355	0.186		35
		CD_3OD				0.399		35
	Yb	CH_3OH			355	0.904		35
		CD_3OD				1.370		35
[Ln(**27a**)(dmf)$_2$(Cl)]	Yb	toluene			355	10		36
[{Ln(**27a**)(dmf)$_n$}$_2${(μ-NC)$_2$Ni(CN)$_2$}]	Yb (n = 2)	toluene			355	1.07		36
	Er (n = 3)	toluene			355	–		36
[{Ln(**27a**)(dmf)$_n$}$_2${(μ-NC)$_2$Pt(CN)$_2$}]	Yb (n = 2)	toluene			355	1.03		36
	Er (n = 3)	toluene			355	–		36
[Ln(**27a**)(μ-$OOCCH_3$)(CH_3OH)]$_2$·$2CHCl_3$	Yb	solid			375	1.27	0.064	37
[Ln(**27a**)($OOCCH_3$)(CH_3OH)$_2$]	Yb	solid			375	1.56	0.078	37
[Ln(**27a**)(η^2-$OOCCH_3$)(4-Me-phen)]·CH_3OH	Yb	solid			375	17.29	0.86	37
[Ln(**27b**)($OOCCH_2CH_3$)(CH_3OH)$_2$]$_2$·$2CH_2Cl_2$	Yb	solid			375	2.40	0.12	37
[Ln(Pt(**27c**))$_3$(tpy)]	Er	thf			400	1.2	0.015	38
[Ln(**28a**)(acac)]	Yb	dmf	400–430	0.13				39
[Ln(**28b**)(acac)]	Yb	dmf	400–430	0.47				39
[Ln(**28c**)(acac)]	Yb	dmf	400–430	0.09				39
[Ln(**28d**)(acac)]	Yb	dmf	400–430	0.06				39
[Ln(**29a**)(acac)]	Yb	dmf	400–430	0.05				39

[Ln(**29b**)(acac)]	Yb	dmf	400–430	0.04				39

Table S1, *continued*

Composition	Ln	State	λ_{exc} / nm	Q^{L}_{Ln} / %	λ_{exc} / nm	τ / µs	Q^{Ln}_{Ln} / %	
[Ln(**29c**)(acac)]	Yb	dmf	400–430	0.03				39
[Ln(**30a**)]	Yb	toluene			514	30 (30) [e]		40
[Ln(**30b**)]	Yb	toluene			514	30 (30) [e]		40
[LnZn(**30b**)]	Yb	toluene			514	30 (30) [e]		40
[LnPd(**30b**)]	Yb	toluene			514	40 (40) [e]		40
[LnPt(**30b**)]	Yb	toluene			514	30 (70) [e]		40
[Ln(**30c**)]	Yb	H_2O			514	10.13		41
[Ln(**31a**)]	Yb	toluene			355	0.26		42
[Ln(**31b**)]	Yb	toluene			355	0.19		42
[Ln(**31c**)]	Yb	toluene			355	0.28		42
[Ln(**31d**)]	Yb	toluene			355	0.35		42
[Ln(**31e**)]	Yb	toluene			355	0.38		42
[Ln(**31f**)]	Yb	toluene			355	0.32		42
[Ln(NO_3)$_3$Zn(**32a**)]	Nd	CH_3CN			355	1.23		43
	Yb	CH_3CN			355	13.40		43
[Ln(NO_3)$_3$Zn(**32b**)]	Nd	CH_3CN			355	1.27		43
	Yb	CH_3CN			355	15.89		43

[a] Formulae of the ligands can be found in Schemes 1-6 and S1 (below). [b] An average lifetime; luminescence decay was fitted using a stretched exponential decay model. [c] The value of 441 µs reported in ref.[10] is erroneous (personal communication from the authors, February 2009). [d] A lower limit estimate due to photochemical decomposition. [e] Lifetime values at 77 K between parentheses.

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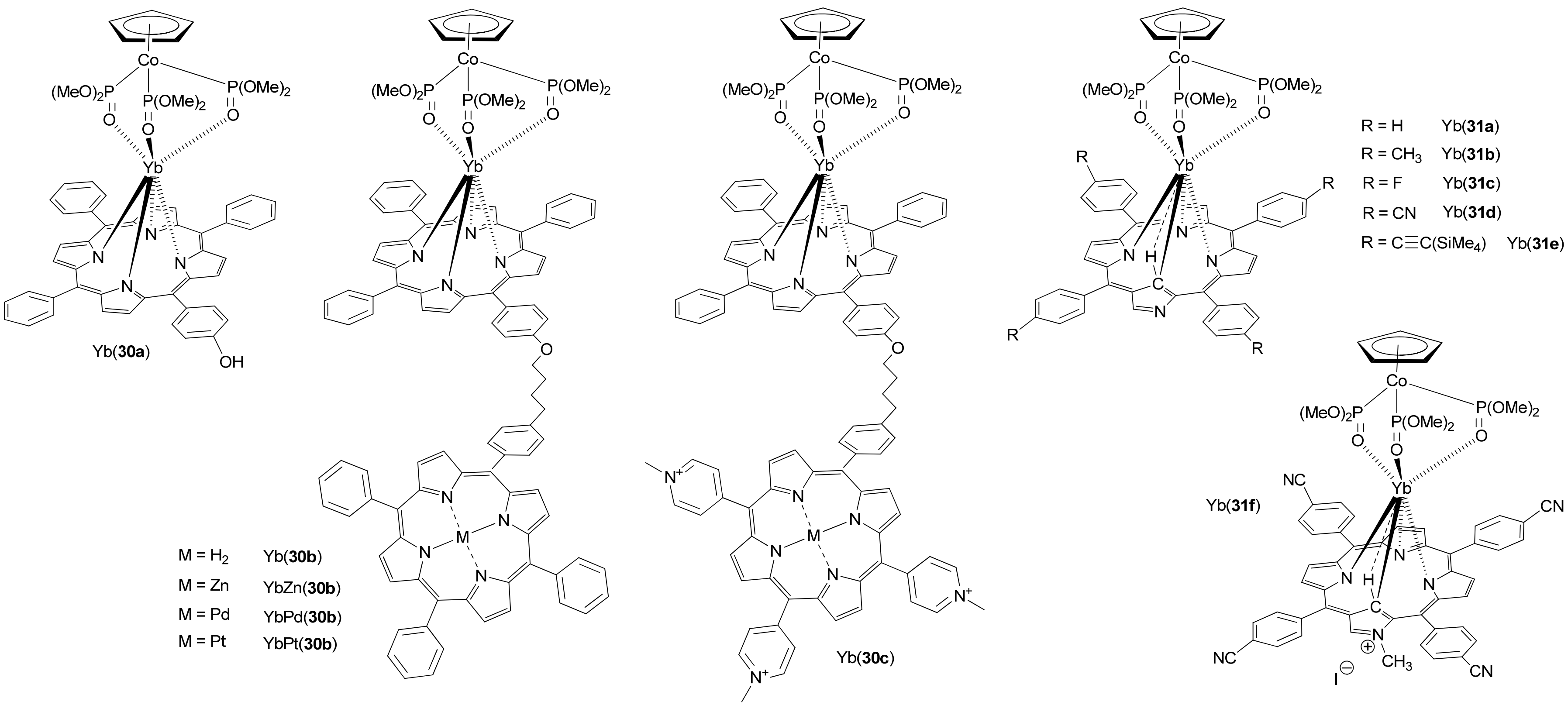

Scheme S1 Ytterbium monoporphyrinates.[40-42]

Table S2 Selected photophysical properties of NIR emitting lanthanide compounds sensitized by transition metals at room temperature: for formulae, see Schemes S2-S3 (below) and 8-11 (main text).

Composition	Ln	State	λ_{exc} / nm	Q_{Ln}^{Ln} / %	τ / µs	d_{av}(M···Ln) / Å	k_{ET} / s^{-1}	Refs.
$PtLn_2$(**33a**)	Yb	CH_2Cl_2	397	0.80	15.9		>10^8	1
		solid	397		14.78			1
Pt_2Ln_4(**33a**)$_2$	Nd	CH_2Cl_2	397				6.07×10^7	1
	Yb	CH_2Cl_2	397	0.77	15.48	14.2	2.12×10^5	1
		solid	397		16.43			1
$PtLn_2$(**33b**)	Yb	CH_2Cl_2	397	0.78	15.5		>10^8	2
		solid	397		13.6			2
$PtLn_2$(**33c**)	Yb	CH_2Cl_2	397	0.73	14.62	14.4	>10^8	2
		solid	397		14.64			3
$PtLn_2$(**33d**)	Yb	CH_2Cl_2	397	0.81	16.1	14.1	>10^8	3
		solid	397		14.8			3
$PtLn_2$(**33e**)	Yb	CH_2Cl_2	397	0.58	11.5	8.6	>10^8	3
		solid	397		12.8			3
$PtLn_2$(**33f**)	Nd	CH_2Cl_2	397				1.24×10^8	3
	Er	CH_2Cl_2	397					3
	Yb	CH_2Cl_2	397	0.64	12.7	14.9	1.4×10^7	3
		solid	397		13.9			3
$PtLn_2$(**33g**)	Yb	CH_2Cl_2	397	0.63	11.8	8.4	>10^8	4
		solid	397		15.1			4
$PtLn_3$(**33h**)	Nd	CH_2Cl_2	397			8.4	5.64×10^7	4
	Yb	CH_2Cl_2	397	0.054	10.9	13.3	2.82×10^6	4
		solid	397		12.5			4
$PtLn_2$(**33i**)	Yb	CH_2Cl_2	397	0.059	11.8		>10^8	5
		solid	397		15.1			5
Pt_6Ln_6(**33j**)	Yb	CH_2Cl_2	397	0.061	12.1	10.5, 16.4, 16.7	1.83×10^5	5
		solid	397		13.1			5
PtLn(**33k**)	Pr	CH_2Cl_2	430		0.2		3×10^8	6
	Nd	CH_2Cl_2	430		0.2		9×10^8	6

	Yb	CH_2Cl_2	430		7.4			6

Table S2, *continued*.

Composition	Ln	State	λ_{exc} / nm	Q_{Ln}^{Ln} / %	τ / µs	d_{av}(M···Ln) / Å	k_{ET} / s^{-1}	Refs.
PtLn(**33l**)	Pr	CH_2Cl_2					1.4×10^8	6
	Nd	CH_2Cl_2					$\approx10^9$	6
[Pt**33m**Ln(tta)$_3$]$_\infty$	Pr	solid	405		0.86		4×10^7	7
	Nd	solid	405		1.02		$>10^8$	7
	Er	solid	405		1.67		4×10^7	7
	Yb	solid	405		9.76	9.9	2×10^6	7
[Pt**33n**Ln(hfa)$_3$]$_\infty$	Nd	solid	405		0.71, 0.54		$>10^8$	7
	Er	solid	405		1.58	9.9	2×10^7	7
	Yb	solid	405		8.24		10^6	7
{Pt**33o**[Ln(tta)$_3$]$_2$}	Nd	CH_2Cl_2	405		1.08		1.4×10^8	7
	Er	CH_2Cl_2	405		1.64		$>10^9$	7
	Yb	CH_2Cl_2	405		11.1	8.3-8.4	$>10^9$	7
Au_4Ln_4(**34a**)	Yb	CH_2Cl_2	397	0.006	11.9	~8.4		8
		solid	397		14.6			8
Au_2Ln_2(**34b**)	Yb	CH_2Cl_2	397	0.006	11.9			8
ReLn(**35a**)	Nd	CH_2Cl_2	430		0.2			6
	Yb	CH_2Cl_2	430		9.0			8
ReLn(**35c**)	Yb	H_2O	337		1.47			9
		D_2O	337		5.30			9
		solid	397		14.4			9
Ir_3Ln(**36a**)[a]	Yb	CH_2Cl_2	337		17.7			10
Ir_2Ln(**36b**)	Yb	CH_3CN	380–490	~0.01	22.1		$>4\times10^8$	11
		solid	380–490	~0.01	17.9			11
RuLn(**37a**)	Nd	solid	450		0.7			12
RuLn(**37b**)	Yb	solid	450		9.8			12
RuLn(**37c**)	Nd	CH_2Cl_2	460			13.4 (max)	2.2×10^6	13
OsLn(**37c**)	Nd	CH_2Cl_2	460				$\approx 10^6$	13
RuLn(**37d**)	Nd	CH_2Cl_2	460	0.004	1.1	15.6 (max)	1.9×10^7	13

Table S2, *continued*.

Composition	Ln	State	λ_{exc} / nm	Q_{Ln}^{Ln} / %	τ / µs	d_{av}(M···Ln) / Å	k_{ET} / s^{-1}	Refs.
	Er	CH_2Cl_2	460				3.3×10^6	13
RuLn(**37d**)	Yb	CH_2Cl_2	460				2.1×10^6	13
OsLn(**37d**)	Nd	CH_2Cl_2	460		1.1	15.6 (max)	7.1×10^6	13
RuLn(**37e**)	Nd	CH_2Cl_2	460			19.9 (max)	1.7×10^6	13

[a] The overall quantum yield of the Yb complex is 0.7 % under excitation at 300 nm.

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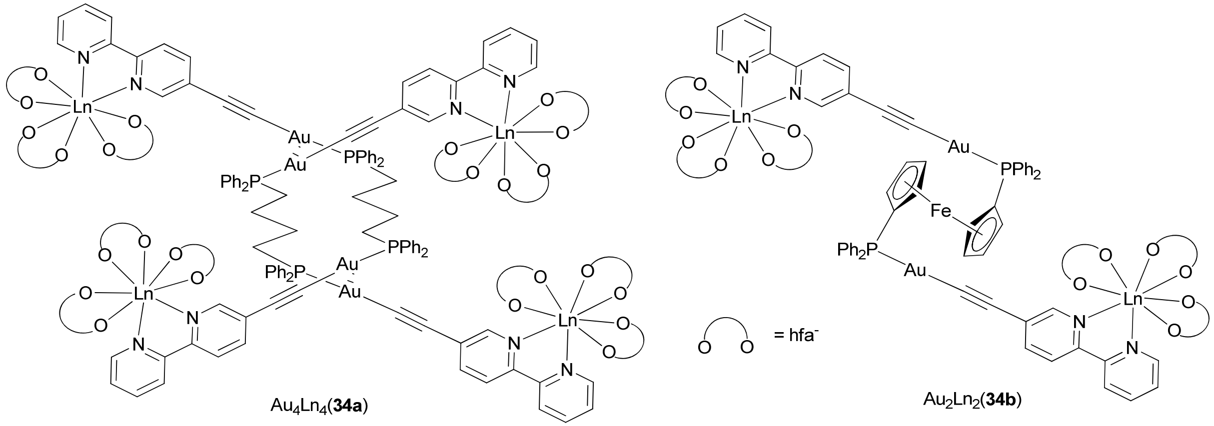
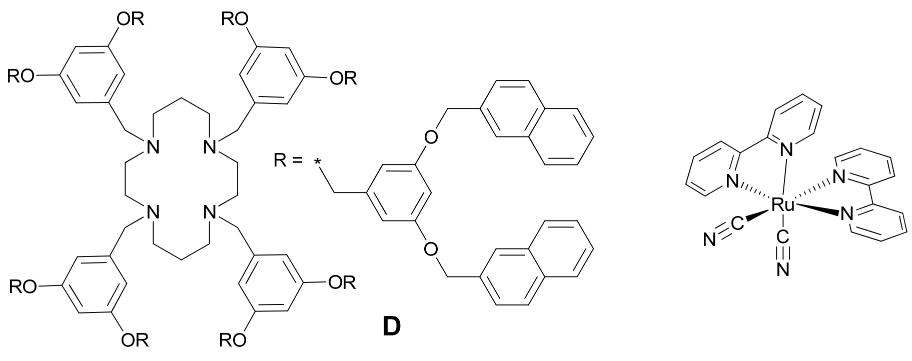


Scheme S2 Au-Ln complexes.



Scheme S3 Structure of the dendrimer **D** forming a three-component self-assembled complex {**D**(Nd)[Ru(bpy)$_2$(CN)$_2$]}.