

**The Influence of Different Cations on the Structure and Spectral Properties of  
Ln<sup>3+</sup> Tetrakis-Complexes with CPh-type Ligand Dimethyl-N-  
trichloroacetylamidophosphate**

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## 1. Theoretical Judd-Ofelt intensity parameters

From the theoretical point of view, the intensity parameters are mainly formed by the forced electric dipole (FED) and dynamic coupling (DC) mechanisms for the 4f-4f intensities when the lanthanide does not occupy a centrosymmetric site [1–4]. The expressions used here for the calculations of the intensity parameters ( $\Omega_{\lambda}^{theo}$ ,  $\lambda = 2, 4, 6$ ) have been described in several references [5–7]. For this reason, a short explanation is given here:

$$\Omega_{\lambda}^{theo} = (2\lambda + 1) \sum_{t,p} \frac{|B_{\lambda tp}|^2}{2t + 1}, \quad B_{\lambda tp} = B_{\lambda tp}^{FED} + B_{\lambda tp}^{DC} \quad S1)$$

where,

$$B_{\lambda tp}^{FED} = \frac{2}{\Delta E} \langle r^{t+1} \rangle \Theta(t, \lambda) \left( \frac{4\pi}{2t+1} \right)^{\frac{1}{2}} \sum_j \frac{e^2 \rho_j g_j (2\beta_j)^{t+1}}{R_j^{t+1}} (Y_p^{t*})_j \quad S2)$$

$$B_{\lambda tp}^{DC} = - \left[ \frac{(\lambda + 1)(2\lambda + 3)}{(2\lambda + 1)} \right]^{\frac{1}{2}} \langle r^{\lambda} \rangle \langle f \| C^{(\lambda)} \| f \rangle \times \left( \frac{4\pi}{2t+1} \right)^{\frac{1}{2}} \sum_j \frac{[(2\beta_j)^{t+1} \alpha_{OPj} + \alpha'_j]}{R_j^{t+1}} (Y_p^{t*})_j \delta_{t, \lambda} \quad S3)$$

with  $t$  and  $p$  being the ranks and components of the spherical harmonics ( $Y_p^{t*}$ ),  $\langle f \| C^{(2)} \| f \rangle = -1.366$ ,  $\langle f \| C^{(4)} \| f \rangle = 1.128$ ,  $\langle f \| C^{(6)} \| f \rangle = -1.27$ ,  $\rho$  is the overlap integral between the valence subshells of the ligating atom and the 4f subshell of the lanthanide ion,  $\beta = 1/(1 \pm \rho)$  is a parameter that defines the centroid of the electronic density of the chemical bond Ln–X (X= ligating atom),  $\alpha'$  is the effective polarizability from each ligand around the Ln<sup>3+</sup> and  $g$  is the charge factor. Both  $\alpha'$  and  $g$  were estimated from fitting procedures in the JOYSpectra program [8]. Eq. S2 stands for the Simple Overlap Model (SOM) [6] for the odd component of the ligand field while Eq. S3 is the Bond Overlap Model (BOM) for the polarizability-dependent term (Dynamic Coupling mechanism) of 4f-4f transitions [7].  $\alpha_{OP}$  are quantities related to the covalent fraction of a chemical bond [7,9–11]. See refs. [7,12,13] for more details on these expressions.

Table S5 summarizes the theoretical intensity parameters and the contribution of the FED mechanism while the values of  $\alpha'$  and  $g$  obtained from the fitting procedure in the JOYSpectra [8] are shown in Table S7.

## 2. Tables

**Table S1.** Crystallographic data and experimental parameters for the NMe<sub>4</sub>[EuL<sub>4</sub>], NEt<sub>4</sub>[EuL<sub>4</sub>], PPh<sub>4</sub>[GdL<sub>4</sub>] structures.

Compound	NMe <sub>4</sub> [EuL <sub>4</sub> ]	NEt <sub>4</sub> [EuL <sub>4</sub> ]	PPh <sub>4</sub> [GdL <sub>4</sub> ]
Formula	C <sub>20</sub> H <sub>36</sub> Cl <sub>12</sub> EuN <sub>5</sub> O <sub>16</sub> P <sub>4</sub>	C <sub>24</sub> H <sub>44</sub> Cl <sub>12</sub> EuN <sub>5</sub> O <sub>16</sub> P <sub>4</sub>	C <sub>40</sub> H <sub>44</sub> Cl <sub>12</sub> GdN <sub>4</sub> O <sub>16</sub> P <sub>5</sub>
<i>D</i> <sub>calc.</sub> / g cm <sup>-3</sup>	1.675	1.684	1.697
<i>m</i> /mm <sup>-1</sup>	2.015	1.947	1.789
Formula Weight	1303.78	1359.88	1574.29
<i>T</i> /K	294	294	173.15
Crystal System		monoclinic	
Space Group	<i>P</i> 2/ <i>n</i>		<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	12.0428(8)	20.4825(6)	19.8828(8)
<i>b</i> /Å	10.2128(6)	12.2546(3)	19.1092(8)
<i>c</i> /Å	21.0833(11)	21.3808(6)	17.3678(6)
<i>a</i> <sup>o</sup>	90	90	90
<i>b</i> <sup>o</sup>	94.501(5)	92.286(2)	110.925(3)
<i>g</i> <sup>o</sup>	90	90	90
V/Å <sup>3</sup>	2585.1(3)	5362.4(2)	6163.6(4)
Z	2	4	4
Measured Refl's.	5084	38874	97953
Indep't Refl's	5084	10526	10860
Refl's I ≥ 2 <i>s</i> (I)	4166	7499	8571
<i>R</i> <sub>int</sub>	.	0.1013	0.1215
Parameters	297	624	711
Goof	1.071	1.053	1.102
<i>wR</i> <sub>2</sub> (all data)	0.1861	0.2276	0.1438
<i>wR</i> <sub>2</sub>	0.1747	0.2035	0.1261
<i>R</i> <sub>1</sub> (all data)	0.0878	0.1061	0.1101
<i>R</i> <sub>1</sub>	0.0725	0.0785	0.0612
CCDC	2290967	2290968	2290969

**Table S2.** Selected bond lengths (Å) in [EuL<sub>4</sub>]<sup>-</sup> and [GdL<sub>4</sub>]<sup>-</sup> anions.

		NMe <sub>4</sub> [EuL <sub>4</sub> ]	NEt <sub>4</sub> [EuL <sub>4</sub> ]	PPh <sub>4</sub> [GdL <sub>4</sub> ]
Ln1	O2	2.343(5)	2.343(5)	2.322(5)
Ln1	O3	2.452(5)	2.492(7)	2.454(5)
Ln1	O4	2.322(5)	2.333(5)	2.337(5)
Ln1	O5	2.500(5)	2.459(5)	2.424(5)
Ln1	O6	2.321(5)	2.351(6)	2.362(5)
Ln1	O7	2.500(5)	2.482(6)	2.415(5)
Ln1	O8	2.343(5)	2.338(5)	2.338(5)
Ln1	O9	2.453(5)	2.433(6)	2.474(5)

The root mean square deviation (RMSD) from the best point group symmetry for the coordination polyhedron of these complexes using the equation:

$$RMSD = \sqrt{\frac{1}{N} \sum_i^N [(x_i - x_i^s)^2 + (y_i - y_i^s)^2 + (z_i - z_i^s)^2]} \quad (S4)$$

where  $N$  is the total number of atoms in the coordination polyhedron (8 for all cases), while  $(x_i, y_i, z_i)$  and  $(x_i^s, y_i^s, z_i^s)$  are the Cartesian coordinates of the actual position of atom  $i$  and its ideal position (exact position within a point group symmetry), respectively.

Table S3 illustrates the deviation to the closest group symmetry for all compounds, as well as the comparison of the coordination polyhedron and the  $[\text{EuL}_4]^-$  unit with each other.

These RMSD values indicate the degree of deviation of the actual coordination polyhedron structures from their idealized symmetries ( $D_{2d}$ ,  $D_2$ , and  $S_4$ ), reflecting how closely the compounds are to their respective point group symmetries. Additionally, these point groups share the  $C_2$  axis symmetry operation. The RMSD for a perfect  $C_2$  operation along the z-axis (Figure S8) shows that larger cations result in higher distortion, which is consistent with the observed hypersensitivity ratios.

**Table S3.** The closest point group symmetry of the coordination polyhedron associated with the number of emission peaks and its deviation (RMSD in Å) from a pure point group symmetry. The RMSD values between structures of the coordination polyhedron and entire  $[\text{EuL}_4]^-$  unit (in parentheses) are also presented.

Compound	Closest point group symmetry	RMSD (Å)
NMe <sub>4</sub> [EuL <sub>4</sub> ]	D <sub>2d</sub>	0.05530
NEt <sub>4</sub> [EuL <sub>4</sub> ]	D <sub>2</sub>	0.05607
PPh <sub>4</sub> [EuL <sub>4</sub> ]	S <sub>4</sub>	0.06189
Compound 1	Compound 2	RMSD (Å)
NMe <sub>4</sub> [EuL <sub>4</sub> ]	NEt <sub>4</sub> [EuL <sub>4</sub> ]	0.05075 (0.75405)
NMe <sub>4</sub> [EuL <sub>4</sub> ]	PPh <sub>4</sub> [EuL <sub>4</sub> ]	0.10009 (2.08243)
NEt <sub>4</sub> [EuL <sub>4</sub> ]	PPh <sub>4</sub> [EuL <sub>4</sub> ]	0.11276 (2.07116)

**Table S4.** Emission decay times (in ms) of Cat[LnL<sub>4</sub>] (Ln = Eu, Tb) measured at

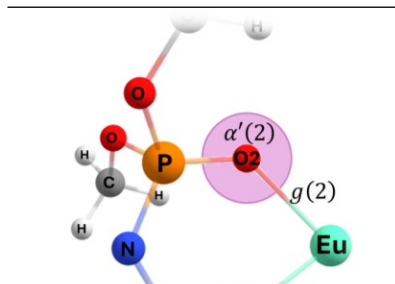
different excitation wavelengths and the deviation of the monoexponential fitting function.

Temperature	298 K			77 K		
	Excitation wavelength (nm)	277 nm	300 nm	394 nm	277 nm	300 nm
NMe <sub>4</sub> [EuL <sub>4</sub> ]		2.62±0.01	2.65±0.01	-	2.72±0.03	2.67±0.04
NEt <sub>4</sub> [EuL <sub>4</sub> ]	-	-	2.78±0.01	-	-	2.76±0.01
PPh <sub>4</sub> [EuL <sub>4</sub> ]	1.45±0.01	-	1.39±0.01	1.43±0.01	-	1.41±0.01
Excitation wavelength (nm)	277 nm	300 nm	368 nm	277 nm	300 nm	368 nm
	NMe <sub>4</sub> [TbL <sub>4</sub> ]	-	2.34±0.01	2.44±0.01	-	2.26±0.02
NEt <sub>4</sub> [TbL <sub>4</sub> ]	-	-	2.90±0.01	-	-	2.66±0.03
PPh <sub>4</sub> [TbL <sub>4</sub> ]	-	-	1.78±0.03	1.58±0.02	-	1.42±0.01

**Table S5.** Theoretical  $\Omega_\lambda$  and the contribution of the FED mechanism (both in units of  $10^{-20} \text{ cm}^2$ ) for Q[LnL<sub>4</sub>] (Q = [NMe<sub>4</sub>]<sup>+</sup>, [NEt<sub>4</sub>]<sup>+</sup>, and [PPh<sub>4</sub>]<sup>+</sup>; Ln = Eu<sup>3+</sup> and Tb<sup>3+</sup>).

[Q] <sup>+</sup>	Q[EuL <sub>4</sub> ]			Q[TbL <sub>4</sub> ]		
	[NMe <sub>4</sub> ] <sup>+</sup>	[NEt <sub>4</sub> ] <sup>+</sup>	[PPh <sub>4</sub> ] <sup>+</sup>	[NMe <sub>4</sub> ] <sup>+</sup>	[NEt <sub>4</sub> ] <sup>+</sup>	[PPh <sub>4</sub> ] <sup>+</sup>
$\Omega_2$ (FED)	4.264 (0.036)	4.556 (0.010)	12.858 (0.013)	3.557 (0.023)	3.716 (0.022)	10.578 (0.008)
$\Omega_4$ (FED)	6.886 (0.312)	6.064 (0.241)	5.784 (0.162)	5.036 (0.165)	6.768 (0.190)	4.315 (0.085)
$\Omega_6$ (FED)	1.912 (0.600)	1.758 (0.463)	1.797 (0.326)	1.111 (0.301)	1.400 (0.371)	1.086 (0.163)

**Table S6.** Values of effective polarizability ( $\alpha'$  in  $\text{\AA}^3$ ) and charge factors  $g$  (dimensionless) obtained for different coordinated oxygen, O=C (1) and O=P (2), as illustrated in the structure fragment below.



	$\alpha'(1)$	$\alpha'(2)$	$g(1)$	$g(2)$
NMe <sub>4</sub> [EuL <sub>4</sub> ]	0.566	0.732	0.881	0.938
NEt <sub>4</sub> [EuL <sub>4</sub> ]	0.354	0.744	0.869	0.774
PPh <sub>4</sub> [EuL <sub>4</sub> ]	0.241	0.899	0.705	0.639

Tables S7–S18 present the energy transfer rates calculated using the JOYSpectra web platform [8] (<http://www.joyspectra.website>). In these tables,  $\Delta$  represents the donor–acceptor energy difference between donor and acceptor transitions.  $W_{d-d}$ ,  $W_{d-m}$ , and  $W_{ex}$  denote the energy transfer by the dipole–dipole, dipole–multipole, and exchange mechanisms, respectively.  $W$  is the sum of all mechanisms for a given pathway ( $p$ ). The forward (ligand-to-Ln) rates perspective,  $W^S$  represents the sum over  $W$  involving the S<sub>1</sub> as a donor, while  $W^T$  is the sum over  $W$  involving the T<sub>1</sub> as a donor state. From the backward (Ln-to-ligand) rates,  $W_b^S$  is the sum over  $W_b$  involving the S<sub>1</sub> as an acceptor, while  $W_b^T$  is the sum over  $W_b$  involving the T<sub>1</sub> as the acceptor state.

**Table S7.** Forward (ligand-to-Eu) IET rates for  $\text{NMe}_4[\text{EuL}_4]$ .

$p$	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_0$	0.0	20707	2.6E-01	1.6E-05	2.6E-01	0.0E+00
2	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_1$	0.2	18973	1.2E+03	0.0E+00	0.0E+00	1.2E+03
3	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_2$	0.0	16517	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5L_6$	1.0	12675	4.7E+03	4.4E+03	3.0E+02	0.0E+00
5	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5G_6$	1.1	11248	5.0E+03	4.6E+03	3.2E+02	0.0E+00
6	$S_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_4$	3.2	10414	1.5E+04	1.6E+03	1.3E+04	0.0E+00
7	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_0$	0.0	21079	8.5E+00	0.0E+00	0.0E+00	8.5E+00
8	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_1$	0.0	19345	4.6E+00	2.8E-04	4.6E+00	4.2E-02
9	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_2$	0.1	16889	3.3E+02	0.0E+00	0.0E+00	3.3E+02
10	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_3$	0.4	14017	1.6E+03	2.6E+00	1.6E+03	0.0E+00
11	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5L_6$	0.0	13047	1.2E+02	1.1E+02	7.9E+00	0.0E+00
12	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5L_7$	0.2	12015	7.4E+02	7.0E+02	4.8E+01	0.0E+00
13	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_2$	91.3	11980	4.2E+05	0.0E+00	0.0E+00	4.2E+05
14	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_3$	2.3	11750	1.0E+04	3.2E+01	1.0E+04	0.0E+00
15	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_6$	0.1	11620	3.0E+02	2.8E+02	1.9E+01	0.0E+00
16	$S_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_5$	0.2	11609	7.2E+02	5.8E+02	1.4E+02	0.0E+00
				$W^S$	4.6 $\times$ 10 <sup>5</sup>			
17	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_0$	0.0	5296	3.6E+02	2.2E-02	3.6E+02	0.0E+00
18	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_1$	84.6	3562	1.2E+09	0.0E+00	0.0E+00	1.2E+09
19	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_2$	0.0	1106	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5L_6$	0.0	-2736	1.9E-04	1.8E-04	1.2E-05	0.0E+00
21	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5G_6$	0.0	-4163	3.6E-08	3.4E-08	2.3E-09	0.0E+00
22	$T_1 \rightarrow S_0$	${}^7F_0 \rightarrow {}^5D_4$	0.0	-4997	7.2E-10	7.6E-11	6.4E-10	0.0E+00
23	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_0$	14.1	5668	2.1E+08	0.0E+00	0.0E+00	2.1E+08
24	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_1$	0.0	3934	7.9E+04	5.2E-02	8.5E+02	7.8E+04
25	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_2$	1.3	1478	1.8E+07	0.0E+00	0.0E+00	1.8E+07
26	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5D_3$	0.0	-1394	2.4E-01	3.9E-04	2.4E-01	0.0E+00
27	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5L_6$	0.0	-2364	4.8E-05	4.5E-05	3.0E-06	0.0E+00
28	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5L_7$	0.0	-3396	5.6E-07	5.3E-07	3.5E-08	0.0E+00
29	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_2$	0.0	-3431	2.6E+00	0.0E+00	0.0E+00	2.6E+00
30	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_3$	0.0	-3661	1.6E-06	4.9E-09	1.6E-06	0.0E+00
31	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_6$	0.0	-3791	2.1E-08	2.0E-08	1.3E-09	0.0E+00
32	$T_1 \rightarrow S_0$	${}^7F_1 \rightarrow {}^5G_5$	0.0	-3802	4.7E-08	3.7E-08	9.1E-09	0.0E+00
				$W^T$	1.5 $\times$ 10 <sup>9</sup>			



**Table S8.** Backward (Eu-to-ligand) IET rates for **NMe<sub>4</sub>[EuL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-20707	1.3E-44	7.6E-49	1.3E-44	0.0E+00
2	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-18973	8.0E-38	0.0E+00	0.0E+00	8.0E-38
3	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-16517	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12675	1.2E-24	1.1E-24	7.6E-26	0.0E+00
5	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.3	-11248	1.2E-21	1.1E-21	7.9E-23	0.0E+00
6	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	70.0	-10414	3.0E-19	3.1E-20	2.7E-19	0.0E+00
7	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-21079	1.0E-42	0.0E+00	0.0E+00	1.0E-42
8	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-19345	8.0E-40	4.8E-44	7.9E-40	7.3E-42
9	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-16889	4.8E-33	0.0E+00	0.0E+00	4.8E-33
10	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-14017	1.8E-26	2.8E-29	1.8E-26	0.0E+00
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13047	7.7E-26	7.2E-26	5.0E-27	0.0E+00
12	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12015	5.9E-23	5.5E-23	3.8E-24	0.0E+00
13	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	28.0	-11980	1.2E-19	0.0E+00	0.0E+00	1.2E-19
14	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	1.5	-11750	6.4E-21	2.0E-23	6.4E-21	0.0E+00
15	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11620	1.9E-22	1.7E-22	1.2E-23	0.0E+00
16	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.1	-11609	5.5E-22	4.4E-22	1.1E-22	0.0E+00
				$W_b^S$	4×10 <sup>-19</sup>			
17	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-5296	3.5E-09	2.1E-13	3.5E-09	0.0E+00
18	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-3562	1.7E+01	0.0E+00	0.0E+00	1.7E+01
19	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-1106	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	2736	9.6E+00	9.0E+00	6.1E-01	0.0E+00
21	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4163	1.8E+00	1.7E+00	1.1E-01	0.0E+00
22	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4997	2.8E+00	3.0E-01	2.5E+00	0.0E+00
23	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-5668	4.9E-03	0.0E+00	0.0E+00	4.9E-03
24	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-3934	2.7E-03	1.8E-09	2.9E-05	2.7E-03
25	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-1478	5.3E+04	0.0E+00	0.0E+00	5.3E+04
26	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	1394	5.2E+02	8.3E-01	5.2E+02	0.0E+00
27	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	2364	6.0E+00	5.7E+00	3.8E-01	0.0E+00
28	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3396	8.8E+00	8.3E+00	5.6E-01	0.0E+00
29	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	100.0	3431	1.4E+08	0.0E+00	0.0E+00	1.4E+08
30	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3661	1.9E+02	5.9E-01	1.9E+02	0.0E+00
31	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3791	2.6E+00	2.4E+00	1.6E-01	0.0E+00
32	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3802	7.1E+00	5.7E+00	1.4E+00	0.0E+00
				$W_b^T$	1.4×10 <sup>8</sup>			

**Table S9.** Forward (ligand-to-Eu) IET rates for  $\text{NEt}_4[\text{EuL}_4]$ .

$p$	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>0</sub>	0.0	20707	6.6E-02	5.2E-06	6.6E-02	0.0E+00
2	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	0.2	18973	1.8E+02	0.0E+00	0.0E+00	1.8E+02
3	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	0.0	16517	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	2.5	12675	1.9E+03	1.9E+03	2.0E+01	0.0E+00
5	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	2.7	11248	2.1E+03	2.0E+03	2.1E+01	0.0E+00
6	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	3.2	10414	2.4E+03	6.5E+02	1.8E+03	0.0E+00
7	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	0.0	21079	1.3E+00	0.0E+00	0.0E+00	1.3E+00
8	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	0.0	19345	1.2E+00	9.2E-05	1.2E+00	6.6E-03
9	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	0.1	16889	5.1E+01	0.0E+00	0.0E+00	5.1E+01
10	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	0.5	14017	4.2E+02	1.1E+00	4.1E+02	0.0E+00
11	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	0.1	13047	5.1E+01	5.0E+01	5.3E-01	0.0E+00
12	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	0.4	12015	3.1E+02	3.1E+02	3.2E+00	0.0E+00
13	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	86.3	11980	6.6E+04	0.0E+00	0.0E+00	6.6E+04
14	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	3.4	11750	2.6E+03	1.3E+01	2.6E+03	0.0E+00
15	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	0.2	11620	1.3E+02	1.2E+02	1.3E+00	0.0E+00
16	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	0.4	11609	2.7E+02	2.5E+02	1.6E+01	0.0E+00
				$W^S$	7.6×10 <sup>4</sup>			
17	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>0</sub>	0.0	4918	9.4E+01	7.6E-03	9.4E+01	0.0E+00
18	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	84.9	3184	1.9E+08	0.0E+00	0.0E+00	1.9E+08
19	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	0.0	728	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	0.0	-3114	1.2E-05	1.2E-05	1.1E-07	0.0E+00
21	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	0.0	-4541	2.1E-09	2.1E-09	2.0E-11	0.0E+00
22	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	0.0	-5375	1.5E-11	4.2E-12	1.1E-11	0.0E+00
23	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	13.8	5290	3.2E+07	0.0E+00	0.0E+00	3.2E+07
24	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	0.0	3556	1.2E+04	1.8E-02	2.2E+02	1.2E+04
25	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	1.2	1100	2.9E+06	0.0E+00	0.0E+00	2.9E+06
26	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	0.0	-1772	9.4E-03	2.5E-05	9.3E-03	0.0E+00
27	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	0.0	-2742	3.0E-06	3.0E-06	2.8E-08	0.0E+00
28	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	0.0	-3774	3.4E-08	3.3E-08	3.1E-10	0.0E+00
29	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	0.0	-3809	5.5E-02	0.0E+00	0.0E+00	5.5E-02
30	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	0.0	-4039	5.6E-08	2.9E-10	5.5E-08	0.0E+00
31	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	0.0	-4169	1.2E-09	1.2E-09	1.1E-11	0.0E+00
32	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	0.0	-4180	2.5E-09	2.3E-09	1.4E-10	0.0E+00
				$W^T$	2.3×10 <sup>8</sup>			

**Table S10.** Backward (Eu-to-ligand) IET rates for **NEt<sub>4</sub>[EuL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-20707	3.2E-45	2.5E-49	3.2E-45	0.0E+00
2	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-18973	1.2E-38	0.0E+00	0.0E+00	1.2E-38
3	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-16517	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12675	4.9E-25	4.9E-25	5.1E-27	0.0E+00
5	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.7	-11248	5.1E-22	5.1E-22	5.3E-24	0.0E+00
6	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	69.6	-10414	4.8E-20	1.3E-20	3.5E-20	0.0E+00
7	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-21079	1.6E-43	0.0E+00	0.0E+00	1.6E-43
8	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-19345	2.0E-40	1.6E-44	2.0E-40	1.1E-42
9	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-16889	7.4E-34	0.0E+00	0.0E+00	7.4E-34
10	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-14017	4.5E-27	1.2E-29	4.5E-27	0.0E+00
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13047	3.2E-26	3.2E-26	3.3E-28	0.0E+00
12	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12015	2.5E-23	2.4E-23	2.6E-25	0.0E+00
13	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	26.9	-11980	1.9E-20	0.0E+00	0.0E+00	1.9E-20
14	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	2.3	-11750	1.6E-21	8.1E-24	1.6E-21	0.0E+00
15	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.1	-11620	7.8E-23	7.7E-23	8.1E-25	0.0E+00
16	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.3	-11609	2.1E-22	2.0E-22	1.3E-23	0.0E+00
				$W_b^S$	$7\times 10^{-20}$			
17	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-4918	5.5E-09	4.5E-13	5.5E-09	0.0E+00
18	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-3184	1.6E+01	0.0E+00	0.0E+00	1.6E+01
19	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-728	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3114	3.7E+00	3.7E+00	3.4E-02	0.0E+00
21	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4541	6.4E-01	6.3E-01	5.9E-03	0.0E+00
22	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	5375	3.6E-01	1.0E-01	2.6E-01	0.0E+00
23	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-5290	4.7E-03	0.0E+00	0.0E+00	4.7E-03
24	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-3556	2.6E-03	3.8E-09	4.7E-05	2.6E-03
25	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.3	-1100	5.1E+04	0.0E+00	0.0E+00	5.1E+04
26	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	1772	1.2E+02	3.3E-01	1.2E+02	0.0E+00
27	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	2742	2.4E+00	2.3E+00	2.2E-02	0.0E+00
28	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3774	3.3E+00	3.3E+00	3.1E-02	0.0E+00
29	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	99.7	3809	1.9E+07	0.0E+00	0.0E+00	1.9E+07
30	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4039	4.2E+01	2.1E-01	4.2E+01	0.0E+00
31	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4169	9.3E-01	9.2E-01	8.7E-03	0.0E+00
32	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4180	2.3E+00	2.2E+00	1.3E-01	0.0E+00
				$W_b^T$	$1.9\times 10^7$			

**Table S11.** Forward (ligand-to-Eu) IET rates for **PPh<sub>4</sub>[EuL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	<i>W</i> (s <sup>-1</sup> )	<i>W</i> <sub><i>d-d</i></sub> (s <sup>-1</sup> )	<i>W</i> <sub><i>d-m</i></sub> (s <sup>-1</sup> )	<i>W</i> <sub><i>ex</i></sub> (s <sup>-1</sup> )
1	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>0</sub>	0.0	17207	6.4E-01	4.5E-05	6.4E-01	0.0E+00
2	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	1.5	15473	2.7E+02	0.0E+00	0.0E+00	2.7E+02
3	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	0.0	13017	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	9.3	9175	1.7E+03	1.7E+03	5.2E-01	0.0E+00
5	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	6.4	7748	1.2E+03	1.2E+03	3.5E-01	0.0E+00
6	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	2.3	6914	4.3E+02	3.0E+02	1.3E+02	0.0E+00
7	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	0.0	17579	3.8E+00	0.0E+00	0.0E+00	3.8E+00
8	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	0.0	15845	7.4E+00	5.2E-04	7.4E+00	1.1E-02
9	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	0.2	13389	4.1E+01	0.0E+00	0.0E+00	4.1E+01
10	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	2.8	10517	5.2E+02	1.4E+00	5.2E+02	0.0E+00
11	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	0.3	9547	5.0E+01	5.0E+01	1.5E-02	0.0E+00
12	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	1.2	8515	2.2E+02	2.2E+02	6.7E-02	0.0E+00
13	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	65.5	8480	1.2E+04	0.0E+00	0.0E+00	1.2E+04
14	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	9.0	8250	1.7E+03	9.0E+00	1.7E+03	0.0E+00
15	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	0.4	8120	8.0E+01	8.0E+01	2.4E-02	0.0E+00
16	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	0.9	8109	1.7E+02	1.6E+02	1.5E+00	0.0E+00
				<i>W</i> <sup>S</sup>	1.8×10 <sup>4</sup>			
17	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>0</sub>	0.0	5497	2.6E+00	1.9E-04	2.6E+00	0.0E+00
18	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	84.9	3763	1.5E+06	0.0E+00	0.0E+00	1.5E+06
19	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	0.0	1307	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	0.0	-2535	7.0E-06	7.0E-06	2.0E-09	0.0E+00
21	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	0.0	-3962	1.3E-09	1.3E-09	3.8E-13	0.0E+00
22	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	0.0	-4796	4.1E-12	2.9E-12	1.2E-12	0.0E+00
23	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	13.8	5869	2.4E+05	0.0E+00	0.0E+00	2.4E+05
24	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	0.0	4135	1.0E+02	4.5E-04	6.3E+00	9.4E+01
25	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	1.3	1679	2.3E+04	0.0E+00	0.0E+00	2.3E+04
26	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	0.0	-1193	4.9E-03	1.4E-05	4.9E-03	0.0E+00
27	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	0.0	-2163	1.7E-06	1.7E-06	5.0E-10	0.0E+00
28	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	0.0	-3195	2.0E-08	2.0E-08	5.9E-12	0.0E+00
29	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	0.0	-3230	8.8E-03	0.0E+00	0.0E+00	8.8E-03
30	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	0.0	-3460	3.3E-08	1.8E-10	3.3E-08	0.0E+00
31	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	0.0	-3590	7.6E-10	7.6E-10	2.2E-13	0.0E+00
32	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	0.0	-3601	1.5E-09	1.5E-09	1.3E-11	0.0E+00
				<i>W</i> <sup>T</sup>	1.8×10 <sup>6</sup>			

**Table S12.** Backward (Eu-to-ligand) IET rates for **PPh<sub>4</sub>[EuL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-17207	6.6E-37	4.7E-41	6.6E-37	0.0E+00
2	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-15473	4.1E-31	0.0E+00	0.0E+00	4.1E-31
3	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13017	0.0E+00	0.0E+00	0.0E+00	0.0E+00
4	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9175	9.4E-18	9.4E-18	2.8E-21	0.0E+00
5	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	2.2	-7748	6.3E-15	6.3E-15	1.9E-18	0.0E+00
6	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →S <sub>1</sub>	63.3	-6914	1.8E-13	1.3E-13	5.6E-14	0.0E+00
7	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-17579	9.9E-36	0.0E+00	0.0E+00	9.9E-36
8	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-15845	2.8E-32	2.0E-36	2.8E-32	4.2E-35
9	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13389	1.3E-26	0.0E+00	0.0E+00	1.3E-26
10	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10517	1.2E-19	3.4E-22	1.2E-19	0.0E+00
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9547	6.8E-19	6.8E-19	2.1E-22	0.0E+00
12	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.1	-8515	3.8E-16	3.8E-16	1.2E-19	0.0E+00
13	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	25.4	-8480	7.4E-14	0.0E+00	0.0E+00	7.4E-14
14	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	7.6	-8250	2.2E-14	1.2E-16	2.2E-14	0.0E+00
15	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.4	-8120	1.1E-15	1.1E-15	3.2E-19	0.0E+00
16	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →S <sub>1</sub>	0.9	-8109	2.7E-15	2.7E-15	2.5E-17	0.0E+00
				$W_b^S$	3×10 <sup>-13</sup>			
17	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-5497	9.6E-12	6.8E-16	9.6E-12	0.0E+00
18	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-3763	7.8E-03	0.0E+00	0.0E+00	7.8E-03
19	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-1307	0.0E+00	0.0E+00	0.0E+00	0.0E+00
20	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	2535	1.3E-01	1.3E-01	3.8E-05	0.0E+00
21	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3962	2.5E-02	2.5E-02	7.1E-06	0.0E+00
22	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>0</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	4796	6.1E-03	4.3E-03	1.8E-03	0.0E+00
23	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-5869	2.2E-06	0.0E+00	0.0E+00	2.2E-06
24	<sup>5</sup> D <sub>1</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-4135	1.3E-06	5.8E-12	8.2E-08	1.2E-06
25	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-1679	2.5E+01	0.0E+00	0.0E+00	2.5E+01
26	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	1193	4.0E+00	1.1E-02	4.0E+00	0.0E+00
27	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	2163	8.2E-02	8.2E-02	2.4E-05	0.0E+00
28	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3195	1.2E-01	1.2E-01	3.5E-05	0.0E+00
29	<sup>5</sup> G <sub>2</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	100.0	3230	1.9E+05	0.0E+00	0.0E+00	1.9E+05
30	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3460	1.5E+00	8.3E-03	1.5E+00	0.0E+00
31	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3590	3.5E-02	3.5E-02	1.0E-05	0.0E+00
32	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>1</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	3601	8.5E-02	8.4E-02	7.4E-04	0.0E+00
				$W_b^T$	1.7×10 <sup>5</sup>			

**Table S13.** Forward (ligand-to-Tb) IET rates for **NMe<sub>4</sub>[TbL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	17556	3.9E+01	4.7E-02	3.9E+01	0.0E+00
2	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>3</sub>	0.0	11764	1.1E+02	6.2E+01	4.5E+01	0.0E+00
3	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	0.2	11577	4.5E+07	5.9E+03	1.3E+05	4.5E+07
4	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>10</sub>	0.0	11029	5.4E+03	5.0E+03	4.6E+02	0.0E+00
5	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>5</sub>	0.1	10233	1.1E+07	2.5E+03	3.5E+05	1.1E+07
6	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>4</sub>	0.0	9713	4.8E+04	2.5E+03	4.6E+04	0.0E+00
7	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>9</sub>	0.0	9592	1.8E+04	1.4E+04	3.8E+03	0.0E+00
8	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>3</sub>	0.0	9023	1.3E+03	7.3E+02	5.3E+02	0.0E+00
9	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>8</sub>	0.0	8810	1.4E+04	1.3E+04	1.2E+03	0.0E+00
10	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>7</sub>	0.0	8543	7.0E+05	8.5E+03	6.9E+05	4.4E+02
11	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>6</sub>	0.1	8330	1.2E+07	0.0E+00	0.0E+00	1.2E+07
12	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>7</sub>	0.2	6621	4.0E+07	0.0E+00	0.0E+00	4.0E+07
13	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>6</sub>	3.7	5109	6.9E+08	0.0E+00	0.0E+00	6.9E+08
14	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>5</sub>	0.0	4233	1.1E+01	0.0E+00	0.0E+00	1.1E+01
15	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>5</sub>	15.8	3066	2.9E+09	0.0E+00	0.0E+00	2.9E+09
16	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>7</sub>	1.0	1411	1.8E+08	0.0E+00	0.0E+00	1.8E+08
17	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>6</sub>	15.1	402	2.8E+09	0.0E+00	0.0E+00	2.8E+09
18	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>5</sub>	1.3	14	2.4E+08	0.0E+00	0.0E+00	2.4E+08
19	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-3334	7.8E-01	0.0E+00	0.0E+00	7.8E-01
20	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>7</sub>	0.0	-3693	1.5E-08	0.0E+00	0.0E+00	1.5E-08
21	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>4</sub>	0.0	19604	1.2E+02	4.6E-03	2.7E+01	9.5E+01
22	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>3</sub>	0.0	13812	4.2E+03	1.6E+01	4.2E+03	0.0E+00
23	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	0.0	13625	7.8E+05	7.0E+01	4.1E+04	7.4E+05
24	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>10</sub>	0.0	13077	1.9E+01	1.8E+01	1.2E+00	0.0E+00
25	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	0.1	12281	1.1E+07	1.9E+02	4.7E+03	1.1E+07
26	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>2</sub>	0.0	11941	6.3E+02	8.4E+01	5.5E+02	0.0E+00
27	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>4</sub>	0.0	11761	2.5E+06	1.0E+02	4.0E+04	2.4E+06
28	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>9</sub>	0.0	11640	1.0E+03	7.7E+02	2.4E+02	0.0E+00
29	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>8</sub>	0.0	10858	3.9E+03	2.6E+03	1.3E+03	0.0E+00
30	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>7</sub>	0.0	10591	5.1E+04	1.0E+03	5.0E+04	0.0E+00
31	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	0.0	10378	3.6E+05	0.0E+00	0.0E+00	3.6E+05
32	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>6</sub>	0.2	7157	3.6E+07	0.0E+00	0.0E+00	3.6E+07
33	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>5</sub>	4.0	6281	7.4E+08	0.0E+00	0.0E+00	7.4E+08
34	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>4</sub>	12.3	5709	2.3E+09	0.0E+00	0.0E+00	2.3E+09
35	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>5</sub>	9.4	5114	1.7E+09	0.0E+00	0.0E+00	1.7E+09
36	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>4</sub>	34.3	4674	6.4E+09	0.0E+00	0.0E+00	6.4E+09
37	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	2.1	2450	3.9E+08	0.0E+00	0.0E+00	3.9E+08
38	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>4</sub>	0.0	2440	3.9E+05	0.0E+00	0.0E+00	3.9E+05
39	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>5</sub>	0.2	2062	2.9E+07	0.0E+00	0.0E+00	2.9E+07
40	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-1286	1.8E+04	0.0E+00	0.0E+00	1.8E+04
				$W^S$	1.8×10 <sup>10</sup>			
41	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	2145	5.6E+02	6.9E-01	5.6E+02	0.0E+00

42	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5D_3$	0.0	-3647	1.8E-08	1.0E-08	7.3E-09	0.0E+00
43	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_6$	0.0	-3834	2.4E+01	3.2E-07	7.0E-06	2.4E+01
44	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_{10}$	0.0	-4382	1.1E-08	9.7E-09	8.7E-10	0.0E+00
45	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_5$	0.0	-5178	1.8E-03	4.1E-11	5.7E-09	1.8E-03
46	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_4$	0.0	-5698	3.5E-11	1.8E-12	3.3E-11	0.0E+00
47	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_9$	0.0	-5819	6.4E-12	5.1E-12	1.3E-12	0.0E+00
48	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_3$	0.0	-6388	1.5E-14	8.7E-15	6.2E-15	0.0E+00
49	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_8$	0.0	-6601	4.7E-14	4.4E-14	3.8E-15	0.0E+00
50	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_7$	0.0	-6868	3.4E-12	5.8E-15	4.7E-13	3.0E-12
51	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_6$	0.0	-7081	2.2E-08	0.0E+00	0.0E+00	2.2E-08
52	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_7$	0.0	-8790	3.1E-12	0.0E+00	0.0E+00	3.1E-12
53	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_6$	0.0	-10302	7.7E-15	0.0E+00	0.0E+00	7.7E-15
54	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_5$	0.0	-11178	7.4E-25	0.0E+00	0.0E+00	7.4E-25
55	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5F_5$	0.0	-12345	2.3E-19	0.0E+00	0.0E+00	2.3E-19
56	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_7$	0.0	-14000	1.0E-24	0.0E+00	0.0E+00	1.0E-24
57	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_6$	0.0	-15009	5.2E-26	0.0E+00	0.0E+00	5.2E-26
58	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_5$	0.0	-15397	4.9E-28	0.0E+00	0.0E+00	4.9E-28
59	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_5$	0.0	-18745	1.0E-37	0.0E+00	0.0E+00	1.0E-37
60	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_7$	0.0	-19104	1.5E-45	0.0E+00	0.0E+00	1.5E-45
61	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_4$	100.0	4193	2.6E+08	1.3E+00	7.3E+03	2.6E+08
62	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_3$	0.0	-1599	1.8E-01	6.7E-04	1.8E-01	0.0E+00
63	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_6$	0.0	-1786	9.8E+04	9.4E-04	5.5E-01	9.8E+04
64	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_{10}$	0.0	-2334	9.0E-06	8.5E-06	5.5E-07	0.0E+00
65	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_5$	0.0	-3130	4.2E+02	7.1E-07	1.8E-05	4.2E+02
66	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_2$	0.0	-3470	3.0E-07	4.1E-08	2.6E-07	0.0E+00
67	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_4$	0.0	-3650	3.9E+00	1.7E-08	6.4E-06	3.9E+00
68	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_9$	0.0	-3771	7.9E-08	6.0E-08	1.9E-08	0.0E+00
69	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_8$	0.0	-4553	2.7E-09	1.8E-09	8.9E-10	0.0E+00
70	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_7$	0.0	-4820	7.1E-09	1.4E-10	7.0E-09	0.0E+00
71	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-5033	1.4E-04	0.0E+00	0.0E+00	1.4E-04
72	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_6$	0.0	-8254	6.5E-11	0.0E+00	0.0E+00	6.5E-11
73	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_5$	0.0	-9130	7.8E-12	0.0E+00	0.0E+00	7.8E-12
74	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_4$	0.0	-9702	8.4E-13	0.0E+00	0.0E+00	8.4E-13
75	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_5$	0.0	-10297	2.0E-14	0.0E+00	0.0E+00	2.0E-14
76	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_4$	0.0	-10737	5.6E-15	0.0E+00	0.0E+00	5.6E-15
77	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-12961	8.7E-22	0.0E+00	0.0E+00	8.7E-22
78	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_4$	0.0	-12971	8.3E-25	0.0E+00	0.0E+00	8.3E-25
79	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_5$	0.0	-13349	7.0E-24	0.0E+00	0.0E+00	7.0E-24
80	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5K_5$	0.0	-16697	1.2E-32	0.0E+00	0.0E+00	1.2E-32
				$W^T$	$2.6 \times 10^8$			

**Table S14.** Backward (Tb-to-ligand) IET rates for  $\text{NMe}_4[\text{TbL}_4]$

$p$	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-17556	9.0E-36	1.1E-38	9.0E-36	0.0E+00
2	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11764	4.4E-23	2.6E-23	1.8E-23	0.0E+00
3	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11577	2.4E-17	3.2E-21	7.2E-20	2.4E-17
4	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11029	2.6E-20	2.4E-20	2.2E-21	0.0E+00
5	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10233	4.8E-15	1.1E-18	1.5E-16	4.6E-15
6	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9713	3.1E-16	1.6E-17	2.9E-16	0.0E+00
7	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9592	9.8E-17	7.7E-17	2.1E-17	0.0E+00
8	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9023	2.9E-16	1.7E-16	1.2E-16	0.0E+00
9	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8810	3.8E-15	3.4E-15	3.0E-16	0.0E+00
10	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8543	7.5E-13	9.3E-15	7.4E-13	4.8E-16
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8330	4.1E-11	0.0E+00	0.0E+00	4.1E-11
12	<sup>5</sup> H <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6621	4.6E-07	0.0E+00	0.0E+00	4.6E-07
13	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5109	1.4E-02	0.0E+00	0.0E+00	1.4E-02
14	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-4233	1.7E-08	0.0E+00	0.0E+00	1.7E-08
15	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-3066	1.3E+03	0.0E+00	0.0E+00	1.3E+03
16	<sup>5</sup> I <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-1411	1.7E+05	0.0E+00	0.0E+00	1.7E+05
17	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	58.9	-402	4.0E+08	0.0E+00	0.0E+00	4.0E+08
18	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	38.4	-14	2.6E+08	0.0E+00	0.0E+00	2.6E+08
19	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	1.3	3334	9.0E+06	0.0E+00	0.0E+00	9.0E+06
20	<sup>5</sup> K <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	3693	7.0E-01	0.0E+00	0.0E+00	7.0E-01
21	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-19604	1.2E-39	4.6E-44	2.7E-40	9.5E-40
22	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13812	7.5E-26	2.8E-28	7.4E-26	0.0E+00
23	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13625	1.8E-23	1.7E-27	9.7E-25	1.7E-23
24	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13077	3.9E-27	3.7E-27	2.4E-28	0.0E+00
25	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12281	2.0E-19	3.4E-24	8.6E-23	2.0E-19
26	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11941	1.3E-22	1.8E-23	1.1E-22	0.0E+00
27	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11761	6.8E-19	2.9E-23	1.1E-20	6.7E-19
28	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11640	2.4E-22	1.8E-22	5.7E-23	0.0E+00
29	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10858	4.4E-20	3.0E-20	1.5E-20	0.0E+00
30	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10591	2.4E-18	4.8E-20	2.3E-18	0.0E+00
31	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10378	5.5E-17	0.0E+00	0.0E+00	5.5E-17
32	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-7157	3.0E-08	0.0E+00	0.0E+00	3.0E-08
33	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6281	5.1E-05	0.0E+00	0.0E+00	5.1E-05
34	<sup>5</sup> H <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5709	3.0E-03	0.0E+00	0.0E+00	3.0E-03
35	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5114	3.4E-02	0.0E+00	0.0E+00	3.4E-02
36	<sup>5</sup> F <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-4674	1.2E+00	0.0E+00	0.0E+00	1.2E+00
37	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2450	2.4E+03	0.0E+00	0.0E+00	2.4E+03
38	<sup>5</sup> I <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2440	3.7E+00	0.0E+00	0.0E+00	3.7E+00
39	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2062	1.4E+03	0.0E+00	0.0E+00	1.4E+03
40	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	1.3	1286	9.0E+06	0.0E+00	0.0E+00	9.0E+06
				$W_b^S$	6.8×10 <sup>8</sup>			
41	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-2145	2.6E-02	3.2E-05	2.6E-02	0.0E+00



42	${}^5\text{D}_3 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	3647	1.4E+00	8.4E-01	6.0E-01	0.0E+00
43	${}^5\text{G}_6 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	45.6	3834	2.6E+09	3.4E+01	7.6E+02	2.6E+09
44	${}^5\text{L}_{10} \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	4382	1.0E+01	9.2E+00	8.3E-01	0.0E+00
45	${}^5\text{G}_5 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	2.7	5178	1.5E+08	3.5E+00	4.8E+02	1.5E+08
46	${}^5\text{G}_4 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	5698	4.4E+01	2.3E+00	4.2E+01	0.0E+00
47	${}^5\text{L}_9 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	5819	6.9E+00	5.4E+00	1.4E+00	0.0E+00
48	${}^5\text{G}_3 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	6388	6.7E-01	3.9E-01	2.8E-01	0.0E+00
49	${}^5\text{L}_8 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	6601	2.5E+00	2.3E+00	2.0E-01	0.0E+00
50	${}^5\text{L}_7 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	6868	7.4E+02	1.2E+00	1.0E+02	6.4E+02
51	${}^5\text{L}_6 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.3	7081	1.6E+07	0.0E+00	0.0E+00	1.6E+07
52	${}^5\text{H}_7 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.1	8790	7.1E+06	0.0E+00	0.0E+00	7.1E+06
53	${}^5\text{H}_6 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.5	10302	3.0E+07	0.0E+00	0.0E+00	3.0E+07
54	${}^5\text{H}_5 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	11178	2.3E-01	0.0E+00	0.0E+00	2.3E-01
55	${}^5\text{F}_5 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.4	12345	2.0E+07	0.0E+00	0.0E+00	2.0E+07
56	${}^5\text{I}_7 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	14000	2.0E+05	0.0E+00	0.0E+00	2.0E+05
57	${}^5\text{I}_6 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	15009	1.5E+06	0.0E+00	0.0E+00	1.5E+06
58	${}^5\text{I}_5 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	15397	1.1E+05	0.0E+00	0.0E+00	1.1E+05
59	${}^5\text{K}_5 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	18745	2.4E+02	0.0E+00	0.0E+00	2.4E+02
60	${}^5\text{K}_7 \rightarrow {}^7\text{F}_6$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	19104	1.4E-05	0.0E+00	0.0E+00	1.4E-05
61	${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	-4193	5.1E-01	2.5E-09	1.4E-05	5.1E-01
62	${}^5\text{D}_3 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	1599	6.2E+02	2.4E+00	6.2E+02	0.0E+00
63	${}^5\text{G}_6 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	8.2	1786	4.6E+08	4.4E+00	2.6E+03	4.6E+08
64	${}^5\text{L}_{10} \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	2334	3.7E-01	3.5E-01	2.2E-02	0.0E+00
65	${}^5\text{G}_5 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	27.0	3130	1.5E+09	2.6E+00	6.4E+01	1.5E+09
66	${}^5\text{D}_2 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	3470	1.2E+01	1.7E+00	1.1E+01	0.0E+00
67	${}^5\text{G}_4 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	3.8	3650	2.1E+08	9.3E-01	3.5E+02	2.1E+08
68	${}^5\text{L}_9 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	3771	3.7E+00	2.8E+00	8.6E-01	0.0E+00
69	${}^5\text{L}_8 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	4553	6.1E+00	4.1E+00	2.0E+00	0.0E+00
70	${}^5\text{L}_7 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	4820	6.6E+01	1.3E+00	6.5E+01	0.0E+00
71	${}^5\text{L}_6 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.1	5033	4.2E+06	0.0E+00	0.0E+00	4.2E+06
72	${}^5\text{H}_6 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.2	8254	1.1E+07	0.0E+00	0.0E+00	1.1E+07
73	${}^5\text{H}_5 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	1.9	9130	1.1E+08	0.0E+00	0.0E+00	1.1E+08
74	${}^5\text{H}_4 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	4.0	9702	2.2E+08	0.0E+00	0.0E+00	2.2E+08
75	${}^5\text{F}_5 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	1.4	10297	7.6E+07	0.0E+00	0.0E+00	7.6E+07
76	${}^5\text{F}_4 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	3.9	10737	2.2E+08	0.0E+00	0.0E+00	2.2E+08
77	${}^5\text{I}_6 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	12961	1.1E+06	0.0E+00	0.0E+00	1.1E+06
78	${}^5\text{I}_4 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	12971	1.6E+03	0.0E+00	0.0E+00	1.6E+03
79	${}^5\text{I}_5 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	13349	6.6E+04	0.0E+00	0.0E+00	6.6E+04
80	${}^5\text{K}_5 \rightarrow {}^7\text{F}_5$	$\text{S}_0 \rightarrow \text{T}_1$	0.0	16697	1.2E+03	0.0E+00	0.0E+00	1.2E+03
				$W_b^T$	$5.6 \times 10^9$			

**Table S15.** Forward (ligand-to-Tb) IET rates for  $\text{NEt}_4[\text{TbL}_4]$ .

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	<i>W</i> (s <sup>-1</sup> )	<i>W</i> <sub><i>d-d</i></sub> (s <sup>-1</sup> )	<i>W</i> <sub><i>d-m</i></sub> (s <sup>-1</sup> )	<i>W</i> <sub><i>ex</i></sub> (s <sup>-1</sup> )
1	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	17556	9.8E+00	2.0E-02	9.8E+00	0.0E+00
2	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>3</sub>	0.0	11764	3.3E+01	2.7E+01	5.7E+00	0.0E+00
3	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	0.2	11577	7.0E+06	2.6E+03	3.3E+04	7.0E+06
4	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>10</sub>	0.0	11029	2.2E+03	2.2E+03	3.9E+01	0.0E+00
5	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>5</sub>	0.1	10233	1.8E+06	1.1E+03	8.8E+04	1.7E+06
6	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>4</sub>	0.0	9713	1.3E+04	1.1E+03	1.2E+04	0.0E+00
7	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>9</sub>	0.0	9592	6.7E+03	6.3E+03	4.5E+02	0.0E+00
8	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>3</sub>	0.0	9023	3.9E+02	3.2E+02	6.7E+01	0.0E+00
9	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>8</sub>	0.0	8810	5.8E+03	5.8E+03	9.6E+01	0.0E+00
10	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>7</sub>	0.0	8543	1.8E+05	3.7E+03	1.7E+05	6.9E+01
11	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>6</sub>	0.1	8330	1.8E+06	0.0E+00	0.0E+00	1.8E+06
12	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>7</sub>	0.2	6621	6.2E+06	0.0E+00	0.0E+00	6.2E+06
13	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>6</sub>	3.7	5109	1.1E+08	0.0E+00	0.0E+00	1.1E+08
14	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>5</sub>	0.0	4233	1.7E+00	0.0E+00	0.0E+00	1.7E+00
15	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>5</sub>	15.8	3066	4.6E+08	0.0E+00	0.0E+00	4.6E+08
16	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>7</sub>	1.0	1411	2.8E+07	0.0E+00	0.0E+00	2.8E+07
17	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>6</sub>	15.1	402	4.4E+08	0.0E+00	0.0E+00	4.4E+08
18	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>5</sub>	1.3	14	3.7E+07	0.0E+00	0.0E+00	3.7E+07
19	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-3334	1.2E-01	0.0E+00	0.0E+00	1.2E-01
20	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>7</sub>	0.0	-3693	2.3E-09	0.0E+00	0.0E+00	2.3E-09
21	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>4</sub>	0.0	19604	2.2E+01	1.9E-03	6.8E+00	1.5E+01
22	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>3</sub>	0.0	13812	1.1E+03	6.8E+00	1.1E+03	0.0E+00
23	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	0.0	13625	1.3E+05	3.0E+01	1.0E+04	1.2E+05
24	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>10</sub>	0.0	13077	7.9E+00	7.8E+00	7.9E-02	0.0E+00
25	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	0.1	12281	1.7E+06	8.2E+01	1.2E+03	1.7E+06
26	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>2</sub>	0.0	11941	1.1E+02	3.5E+01	7.2E+01	0.0E+00
27	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>4</sub>	0.0	11761	3.9E+05	4.6E+01	1.0E+04	3.8E+05
28	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>9</sub>	0.0	11640	3.7E+02	3.4E+02	2.9E+01	0.0E+00
29	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>8</sub>	0.0	10858	1.3E+03	1.1E+03	1.6E+02	0.0E+00
30	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>7</sub>	0.0	10591	1.3E+04	4.5E+02	1.3E+04	0.0E+00
31	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	0.0	10378	5.7E+04	0.0E+00	0.0E+00	5.7E+04
32	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>6</sub>	0.2	7157	5.6E+06	0.0E+00	0.0E+00	5.6E+06
33	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>5</sub>	4.0	6281	1.2E+08	0.0E+00	0.0E+00	1.2E+08
34	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>4</sub>	12.3	5709	3.6E+08	0.0E+00	0.0E+00	3.6E+08
35	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>5</sub>	9.4	5114	2.7E+08	0.0E+00	0.0E+00	2.7E+08
36	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>4</sub>	34.3	4674	9.9E+08	0.0E+00	0.0E+00	9.9E+08
37	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	2.1	2450	6.0E+07	0.0E+00	0.0E+00	6.0E+07
38	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>4</sub>	0.0	2440	6.1E+04	0.0E+00	0.0E+00	6.1E+04
39	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>5</sub>	0.2	2062	4.5E+06	0.0E+00	0.0E+00	4.5E+06
40	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-1286	2.8E+03	0.0E+00	0.0E+00	2.8E+03
				<i>W</i> <sup>S</sup>	2.9×10 <sup>9</sup>			
41	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	1767	1.5E+02	3.1E-01	1.4E+02	0.0E+00

42	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5D_3$	0.0	-4025	7.6E-10	6.4E-10	1.2E-10	0.0E+00
43	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_6$	0.0	-4212	4.9E-01	1.9E-08	2.4E-07	4.9E-01
44	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_{10}$	0.0	-4760	5.9E-10	5.8E-10	9.5E-12	0.0E+00
45	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_5$	0.0	-5556	3.4E-05	2.3E-12	1.8E-10	3.4E-05
46	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_4$	0.0	-6076	1.1E-12	9.9E-14	1.0E-12	0.0E+00
47	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_9$	0.0	-6197	3.0E-13	2.8E-13	1.8E-14	0.0E+00
48	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_3$	0.0	-6766	5.5E-16	4.6E-16	8.9E-17	0.0E+00
49	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_8$	0.0	-6979	2.3E-15	2.3E-15	3.5E-17	0.0E+00
50	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_7$	0.0	-7246	6.5E-14	3.0E-16	1.3E-14	5.2E-14
51	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_6$	0.0	-7459	3.8E-10	0.0E+00	0.0E+00	3.8E-10
52	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_7$	0.0	-9168	4.6E-14	0.0E+00	0.0E+00	4.6E-14
53	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_6$	0.0	-10680	9.9E-17	0.0E+00	0.0E+00	9.9E-17
54	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_5$	0.0	-11556	8.7E-27	0.0E+00	0.0E+00	8.7E-27
55	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5F_5$	0.0	-12723	2.4E-21	0.0E+00	0.0E+00	2.4E-21
56	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_7$	0.0	-14378	8.9E-27	0.0E+00	0.0E+00	8.9E-27
57	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_6$	0.0	-15387	3.9E-28	0.0E+00	0.0E+00	3.9E-28
58	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_5$	0.0	-15775	3.4E-30	0.0E+00	0.0E+00	3.4E-30
59	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_5$	0.0	-19123	4.5E-40	0.0E+00	0.0E+00	4.5E-40
60	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_7$	0.0	-19482	6.1E-48	0.0E+00	0.0E+00	6.1E-48
61	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_4$	100.0	3815	4.0E+07	5.4E-01	1.9E+03	4.0E+07
62	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_3$	0.0	-1977	6.8E-03	4.4E-05	6.7E-03	0.0E+00
63	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_6$	0.0	-2164	2.3E+03	6.3E-05	2.1E-02	2.3E+03
64	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_{10}$	0.0	-2712	5.7E-07	5.6E-07	5.1E-09	0.0E+00
65	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_5$	0.0	-3508	9.1E+00	4.5E-08	6.4E-07	9.1E+00
66	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_2$	0.0	-3848	7.1E-09	2.4E-09	4.7E-09	0.0E+00
67	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_4$	0.0	-4028	8.3E-02	1.1E-09	2.3E-07	8.3E-02
68	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_9$	0.0	-4149	4.0E-09	3.7E-09	3.0E-10	0.0E+00
69	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_8$	0.0	-4931	1.2E-10	1.1E-10	1.4E-11	0.0E+00
70	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_7$	0.0	-5198	2.4E-10	8.5E-12	2.3E-10	0.0E+00
71	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-5411	2.8E-06	0.0E+00	0.0E+00	2.8E-06
72	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_6$	0.0	-8632	1.0E-12	0.0E+00	0.0E+00	1.0E-12
73	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_5$	0.0	-9508	1.1E-13	0.0E+00	0.0E+00	1.1E-13
74	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_4$	0.0	-10080	1.2E-14	0.0E+00	0.0E+00	1.2E-14
75	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_5$	0.0	-10675	2.6E-16	0.0E+00	0.0E+00	2.6E-16
76	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_4$	0.0	-11115	6.9E-17	0.0E+00	0.0E+00	6.9E-17
77	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-13339	8.4E-24	0.0E+00	0.0E+00	8.4E-24
78	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_4$	0.0	-13349	8.0E-27	0.0E+00	0.0E+00	8.0E-27
79	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_5$	0.0	-13727	6.4E-26	0.0E+00	0.0E+00	6.4E-26
80	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5K_5$	0.0	-17075	6.9E-35	0.0E+00	0.0E+00	6.9E-35
				$W^T$	$4.0 \times 10^7$			

**Table S16.** Backward (Tb-to-ligand) IET rates for  $\text{NEt}_4[\text{TbL}_4]$ .

$p$	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-17556	2.3E-36	4.7E-39	2.3E-36	0.0E+00
2	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11764	1.4E-23	1.1E-23	2.3E-24	0.0E+00
3	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11577	3.8E-18	1.4E-21	1.8E-20	3.8E-18
4	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11029	1.1E-20	1.0E-20	1.8E-22	0.0E+00
5	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10233	7.6E-16	4.6E-19	3.7E-17	7.2E-16
6	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9713	8.0E-17	6.9E-18	7.4E-17	0.0E+00
7	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9592	3.6E-17	3.4E-17	2.4E-18	0.0E+00
8	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9023	8.9E-17	7.3E-17	1.5E-17	0.0E+00
9	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8810	1.5E-15	1.5E-15	2.5E-17	0.0E+00
10	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8543	1.9E-13	4.1E-15	1.9E-13	7.4E-17
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8330	6.4E-12	0.0E+00	0.0E+00	6.4E-12
12	<sup>5</sup> H <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6621	7.2E-08	0.0E+00	0.0E+00	7.2E-08
13	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5109	2.1E-03	0.0E+00	0.0E+00	2.1E-03
14	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-4233	2.7E-09	0.0E+00	0.0E+00	2.7E-09
15	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-3066	2.0E+02	0.0E+00	0.0E+00	2.0E+02
16	<sup>5</sup> I <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-1411	2.7E+04	0.0E+00	0.0E+00	2.7E+04
17	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	58.9	-402	6.3E+07	0.0E+00	0.0E+00	6.3E+07
18	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	38.4	-14	4.1E+07	0.0E+00	0.0E+00	4.1E+07
19	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	1.3	3334	1.4E+06	0.0E+00	0.0E+00	1.4E+06
20	<sup>5</sup> K <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	3693	1.1E-01	0.0E+00	0.0E+00	1.1E-01
21	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-19604	2.2E-40	1.9E-44	6.8E-41	1.5E-40
22	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13812	1.9E-26	1.2E-28	1.9E-26	0.0E+00
23	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13625	3.0E-24	7.2E-28	2.5E-25	2.7E-24
24	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-13077	1.6E-27	1.6E-27	1.6E-29	0.0E+00
25	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-12281	3.2E-20	1.5E-24	2.2E-23	3.2E-20
26	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11941	2.2E-23	7.3E-24	1.5E-23	0.0E+00
27	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11761	1.1E-19	1.3E-23	2.8E-21	1.0E-19
28	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-11640	8.6E-23	7.9E-23	6.7E-24	0.0E+00
29	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10858	1.5E-20	1.3E-20	1.8E-21	0.0E+00
30	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10591	6.1E-19	2.1E-20	5.9E-19	0.0E+00
31	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10378	8.5E-18	0.0E+00	0.0E+00	8.5E-18
32	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-7157	4.7E-09	0.0E+00	0.0E+00	4.7E-09
33	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6281	8.0E-06	0.0E+00	0.0E+00	8.0E-06
34	<sup>5</sup> H <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5709	4.7E-04	0.0E+00	0.0E+00	4.7E-04
35	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5114	5.2E-03	0.0E+00	0.0E+00	5.2E-03
36	<sup>5</sup> F <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-4674	1.9E-01	0.0E+00	0.0E+00	1.9E-01
37	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2450	3.7E+02	0.0E+00	0.0E+00	3.7E+02
38	<sup>5</sup> I <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2440	5.7E-01	0.0E+00	0.0E+00	5.7E-01
39	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2062	2.1E+02	0.0E+00	0.0E+00	2.1E+02
40	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	1.3	1286	1.4E+06	0.0E+00	0.0E+00	1.4E+06
				$W_b^S$	1.1×10 <sup>8</sup>			
41	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-1767	4.1E-02	8.8E-05	4.1E-02	0.0E+00

42	${}^5D_3 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	4025	3.9E-01	3.2E-01	6.3E-02	0.0E+00
43	${}^5G_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	47.1	4212	3.3E+08	1.3E+01	1.6E+02	3.3E+08
44	${}^5L_{10} \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	4760	3.5E+00	3.4E+00	5.5E-02	0.0E+00
45	${}^5G_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	2.5	5556	1.8E+07	1.2E+00	9.6E+01	1.8E+07
46	${}^5G_4 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6076	8.9E+00	7.8E-01	8.1E+00	0.0E+00
47	${}^5L_9 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6197	2.0E+00	1.8E+00	1.2E-01	0.0E+00
48	${}^5G_3 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6766	1.5E-01	1.3E-01	2.5E-02	0.0E+00
49	${}^5L_8 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6979	7.5E-01	7.3E-01	1.1E-02	0.0E+00
50	${}^5L_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	7246	8.7E+01	3.9E-01	1.8E+01	6.8E+01
51	${}^5L_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.2	7459	1.6E+06	0.0E+00	0.0E+00	1.6E+06
52	${}^5H_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.1	9168	6.5E+05	0.0E+00	0.0E+00	6.5E+05
53	${}^5H_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.3	10680	2.4E+06	0.0E+00	0.0E+00	2.4E+06
54	${}^5H_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	11556	1.7E-02	0.0E+00	0.0E+00	1.7E-02
55	${}^5F_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.2	12723	1.3E+06	0.0E+00	0.0E+00	1.3E+06
56	${}^5I_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	14378	1.0E+04	0.0E+00	0.0E+00	1.0E+04
57	${}^5I_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	15387	6.8E+04	0.0E+00	0.0E+00	6.8E+04
58	${}^5I_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	15775	4.7E+03	0.0E+00	0.0E+00	4.7E+03
59	${}^5K_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	19123	6.3E+00	0.0E+00	0.0E+00	6.3E+00
60	${}^5K_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	19482	3.5E-07	0.0E+00	0.0E+00	3.5E-07
61	${}^5D_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	-3815	4.9E-01	6.6E-09	2.3E-05	4.9E-01
62	${}^5D_3 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	1977	1.5E+02	9.7E-01	1.5E+02	0.0E+00
63	${}^5G_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	9.3	2164	6.6E+07	1.8E+00	6.1E+02	6.6E+07
64	${}^5L_{10} \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	2712	1.4E-01	1.4E-01	1.3E-03	0.0E+00
65	${}^5G_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	28.9	3508	2.0E+08	1.0E+00	1.4E+01	2.0E+08
66	${}^5D_2 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	3848	1.8E+00	6.2E-01	1.2E+00	0.0E+00
67	${}^5G_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	4.0	4028	2.8E+07	3.6E-01	7.7E+01	2.8E+07
68	${}^5L_9 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	4149	1.2E+00	1.1E+00	8.5E-02	0.0E+00
69	${}^5L_8 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	4931	1.7E+00	1.5E+00	2.0E-01	0.0E+00
70	${}^5L_7 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	5198	1.4E+01	4.8E-01	1.3E+01	0.0E+00
71	${}^5L_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.1	5411	5.1E+05	0.0E+00	0.0E+00	5.1E+05
72	${}^5H_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.2	8632	1.1E+06	0.0E+00	0.0E+00	1.1E+06
73	${}^5H_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	1.4	9508	9.5E+06	0.0E+00	0.0E+00	9.5E+06
74	${}^5H_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	2.7	10080	1.9E+07	0.0E+00	0.0E+00	1.9E+07
75	${}^5F_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.9	10675	6.1E+06	0.0E+00	0.0E+00	6.1E+06
76	${}^5F_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	2.3	11115	1.7E+07	0.0E+00	0.0E+00	1.7E+07
77	${}^5I_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	13339	6.4E+04	0.0E+00	0.0E+00	6.4E+04
78	${}^5I_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	13349	9.3E+01	0.0E+00	0.0E+00	9.3E+01
79	${}^5I_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	13727	3.8E+03	0.0E+00	0.0E+00	3.8E+03
80	${}^5K_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	17075	4.2E+01	0.0E+00	0.0E+00	4.2E+01
				$W_b^T$	$7.1 \times 10^8$			

**Table S17.** Forward (ligand-to-Tb) IET rates for **PPh<sub>4</sub>[TbL<sub>4</sub>]**.

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	14056	3.6E+01	8.0E-02	3.6E+01	0.0E+00
2	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>3</sub>	0.0	8264	1.9E+01	1.8E+01	6.0E-01	0.0E+00
3	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	2.5	8077	1.1E+06	1.7E+03	2.0E+04	1.1E+06
4	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>10</sub>	0.0	7529	1.2E+03	1.2E+03	1.8E+00	0.0E+00
5	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>5</sub>	0.5	6733	2.2E+05	4.7E+02	3.6E+04	1.8E+05
6	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>4</sub>	0.0	6213	4.4E+03	3.9E+02	4.0E+03	0.0E+00
7	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>9</sub>	0.0	6092	2.2E+03	2.2E+03	2.3E+01	0.0E+00
8	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>3</sub>	0.0	5523	9.8E+01	9.5E+01	3.1E+00	0.0E+00
9	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>8</sub>	0.0	5310	1.6E+03	1.6E+03	2.2E+00	0.0E+00
10	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>7</sub>	0.1	5043	4.3E+04	9.5E+02	4.2E+04	4.4E+00
11	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>6</sub>	0.2	4830	1.1E+05	0.0E+00	0.0E+00	1.1E+05
12	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>7</sub>	0.5	3121	2.2E+05	0.0E+00	0.0E+00	2.2E+05
13	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>6</sub>	5.5	1609	2.5E+06	0.0E+00	0.0E+00	2.5E+06
14	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>5</sub>	0.0	733	3.0E-02	0.0E+00	0.0E+00	3.0E-02
15	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>5</sub>	1.5	-434	6.9E+05	0.0E+00	0.0E+00	6.9E+05
16	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>7</sub>	0.0	-2089	8.7E+00	0.0E+00	0.0E+00	8.7E+00
17	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>6</sub>	0.0	-3098	7.7E-01	0.0E+00	0.0E+00	7.7E-01
18	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>5</sub>	0.0	-3486	8.9E-03	0.0E+00	0.0E+00	8.9E-03
19	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-6834	9.9E-12	0.0E+00	0.0E+00	9.9E-12
20	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> K <sub>7</sub>	0.0	-7193	1.7E-19	0.0E+00	0.0E+00	1.7E-19
21	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>4</sub>	0.0	16104	7.4E+01	1.3E-02	4.7E+01	2.7E+01
22	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>3</sub>	0.0	10312	1.3E+03	8.6E+00	1.2E+03	0.0E+00
23	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	0.1	10125	4.7E+04	3.6E+01	1.2E+04	3.5E+04
24	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>10</sub>	0.0	9577	7.9E+00	7.9E+00	2.3E-03	0.0E+00
25	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	0.8	8781	3.5E+05	6.5E+01	8.8E+02	3.5E+05
26	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>2</sub>	0.0	8441	3.4E+01	2.5E+01	8.4E+00	0.0E+00
27	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>4</sub>	0.2	8261	7.1E+04	3.1E+01	6.5E+03	6.5E+04
28	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>9</sub>	0.0	8140	2.2E+02	2.2E+02	2.8E+00	0.0E+00
29	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>8</sub>	0.0	7358	6.0E+02	5.9E+02	1.3E+01	0.0E+00
30	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>7</sub>	0.0	7091	5.9E+03	2.1E+02	5.6E+03	0.0E+00
31	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	0.0	6878	6.4E+03	0.0E+00	0.0E+00	6.4E+03
32	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>6</sub>	0.5	3657	2.4E+05	0.0E+00	0.0E+00	2.4E+05
33	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>5</sub>	8.3	2781	3.8E+06	0.0E+00	0.0E+00	3.8E+06
34	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>4</sub>	21.5	2209	9.7E+06	0.0E+00	0.0E+00	9.7E+06
35	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>5</sub>	13.8	1614	6.2E+06	0.0E+00	0.0E+00	6.2E+06
36	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>4</sub>	43.9	1174	2.0E+07	0.0E+00	0.0E+00	2.0E+07
37	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	0.0	-1050	3.9E+03	0.0E+00	0.0E+00	3.9E+03
38	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>4</sub>	0.0	-1060	3.7E+00	0.0E+00	0.0E+00	3.7E+00
39	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>5</sub>	0.0	-1438	3.9E+01	0.0E+00	0.0E+00	3.9E+01
40	S <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> K <sub>5</sub>	0.0	-4786	4.3E-07	0.0E+00	0.0E+00	4.3E-07
				$W^S$	4.5×10 <sup>7</sup>			
41	T <sub>1</sub> →S <sub>0</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	0.0	2346	4.2E+00	9.3E-03	4.2E+00	0.0E+00

42	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5D_3$	0.0	-3446	4.1E-10	4.0E-10	1.3E-11	0.0E+00
43	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_6$	0.0	-3633	8.1E-02	1.2E-08	1.5E-07	8.1E-02
44	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_{10}$	0.0	-4181	3.8E-10	3.8E-10	5.7E-13	0.0E+00
45	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_5$	0.0	-4977	6.2E-06	1.6E-12	1.2E-10	6.2E-06
46	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_4$	0.0	-5497	7.8E-13	7.1E-14	7.1E-13	0.0E+00
47	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_9$	0.0	-5618	2.0E-13	2.0E-13	2.0E-15	0.0E+00
48	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5G_3$	0.0	-6187	3.6E-16	3.4E-16	1.1E-17	0.0E+00
49	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_8$	0.0	-6400	1.7E-15	1.7E-15	2.3E-18	0.0E+00
50	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_7$	0.0	-6667	2.1E-14	2.3E-16	1.0E-14	1.1E-14
51	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5L_6$	0.0	-6880	8.0E-11	0.0E+00	0.0E+00	8.0E-11
52	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_7$	0.0	-8589	1.1E-14	0.0E+00	0.0E+00	1.1E-14
53	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_6$	0.0	-10101	2.8E-17	0.0E+00	0.0E+00	2.8E-17
54	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5H_5$	0.0	-10977	2.7E-27	0.0E+00	0.0E+00	2.7E-27
55	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5F_5$	0.0	-12144	8.6E-22	0.0E+00	0.0E+00	8.6E-22
56	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_7$	0.0	-13799	3.9E-27	0.0E+00	0.0E+00	3.9E-27
57	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_6$	0.0	-14808	2.0E-28	0.0E+00	0.0E+00	2.0E-28
58	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5I_5$	0.0	-15196	1.8E-30	0.0E+00	0.0E+00	1.8E-30
59	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_5$	0.0	-18544	4.0E-40	0.0E+00	0.0E+00	4.0E-40
60	$T_1 \rightarrow S_0$	${}^7F_6 \rightarrow {}^5K_7$	0.0	-18903	5.8E-48	0.0E+00	0.0E+00	5.8E-48
61	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_4$	99.9	4394	3.1E+05	1.5E-02	5.3E+01	3.1E+05
62	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_3$	0.0	-1398	3.6E-03	2.5E-05	3.6E-03	0.0E+00
63	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_6$	0.1	-1585	3.3E+02	3.5E-05	1.1E-02	3.3E+02
64	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_{10}$	0.0	-2133	3.2E-07	3.2E-07	9.0E-11	0.0E+00
65	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_5$	0.0	-2929	1.4E+00	2.7E-08	3.7E-07	1.4E+00
66	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5D_2$	0.0	-3269	2.0E-09	1.5E-09	4.9E-10	0.0E+00
67	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5G_4$	0.0	-3449	1.3E-02	6.5E-10	1.4E-07	1.3E-02
68	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_9$	0.0	-3570	2.4E-09	2.3E-09	2.9E-11	0.0E+00
69	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_8$	0.0	-4352	7.3E-11	7.1E-11	1.5E-12	0.0E+00
70	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5L_7$	0.0	-4619	1.5E-10	5.7E-12	1.5E-10	0.0E+00
71	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-4832	4.9E-07	0.0E+00	0.0E+00	4.9E-07
72	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_6$	0.0	-8053	2.4E-13	0.0E+00	0.0E+00	2.4E-13
73	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_5$	0.0	-8929	2.8E-14	0.0E+00	0.0E+00	2.8E-14
74	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5H_4$	0.0	-9501	3.1E-15	0.0E+00	0.0E+00	3.1E-15
75	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_5$	0.0	-10096	7.3E-17	0.0E+00	0.0E+00	7.3E-17
76	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5F_4$	0.0	-10536	2.1E-17	0.0E+00	0.0E+00	2.1E-17
77	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_6$	0.0	-12760	3.3E-24	0.0E+00	0.0E+00	3.3E-24
78	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_4$	0.0	-12770	3.1E-27	0.0E+00	0.0E+00	3.1E-27
79	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5I_5$	0.0	-13148	2.6E-26	0.0E+00	0.0E+00	2.6E-26
80	$T_1 \rightarrow S_0$	${}^7F_5 \rightarrow {}^5K_5$	0.0	-16496	4.5E-35	0.0E+00	0.0E+00	4.5E-35
				$W^T$	$3.1 \times 10^5$			

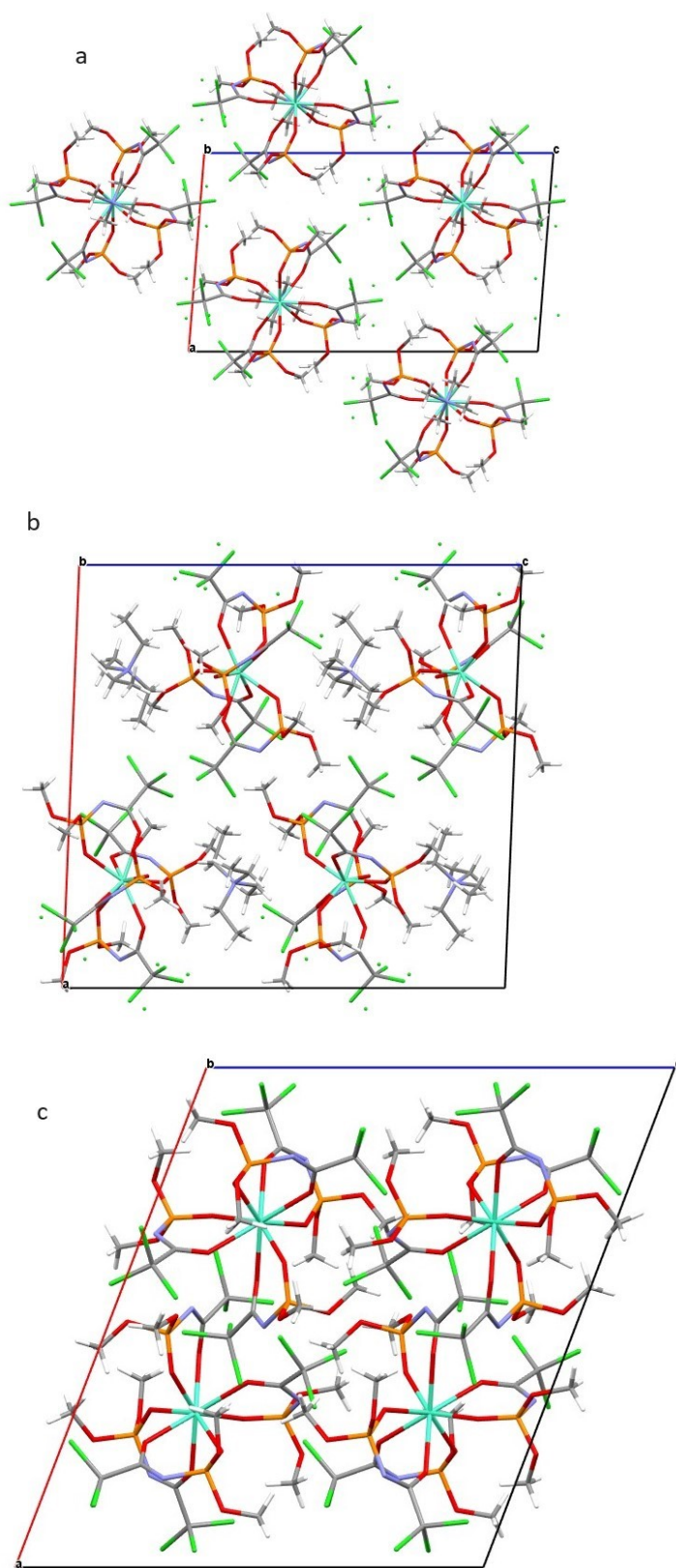
**Table S18.** Backward (Tb-to-ligand) IET rates for **PPh<sub>4</sub>[TbL<sub>4</sub>]**

<i>p</i>	donor	acceptor	contr. (%)	$\Delta$ (cm <sup>-1</sup> )	$W_b$ (s <sup>-1</sup> )	$W_{d-d}$ (s <sup>-1</sup> )	$W_{d-m}$ (s <sup>-1</sup> )	$W_{ex}$ (s <sup>-1</sup> )
1	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-14056	1.8E-28	4.0E-31	1.8E-28	0.0E+00
2	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8264	1.7E-16	1.6E-16	5.4E-18	0.0E+00
3	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8077	1.4E-11	2.0E-14	2.4E-13	1.3E-11
4	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-7529	1.2E-13	1.2E-13	1.9E-16	0.0E+00
5	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6733	2.0E-09	4.3E-12	3.3E-10	1.7E-09
6	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6213	6.0E-10	5.4E-11	5.5E-10	0.0E+00
7	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6092	2.6E-10	2.6E-10	2.6E-12	0.0E+00
8	<sup>5</sup> G <sub>3</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5523	4.8E-10	4.7E-10	1.5E-11	0.0E+00
9	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5310	9.1E-09	9.0E-09	1.2E-11	0.0E+00
10	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-5043	1.0E-06	2.2E-08	9.8E-07	1.0E-10
11	<sup>5</sup> L <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-4830	8.4E-06	0.0E+00	0.0E+00	8.4E-06
12	<sup>5</sup> H <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-3121	5.6E-02	0.0E+00	0.0E+00	5.6E-02
13	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-1609	1.0E+03	0.0E+00	0.0E+00	1.0E+03
14	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-733	1.0E-03	0.0E+00	0.0E+00	1.0E-03
15	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	65.8	434	6.6E+06	0.0E+00	0.0E+00	6.6E+06
16	<sup>5</sup> I <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	1.8	2089	1.8E+05	0.0E+00	0.0E+00	1.8E+05
17	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	23.8	3098	2.4E+06	0.0E+00	0.0E+00	2.4E+06
18	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	2.1	3486	2.1E+05	0.0E+00	0.0E+00	2.1E+05
19	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	6834	2.5E+03	0.0E+00	0.0E+00	2.5E+03
20	<sup>5</sup> K <sub>7</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	7193	1.7E-04	0.0E+00	0.0E+00	1.7E-04
21	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-16104	1.6E-32	2.9E-36	1.0E-32	5.9E-33
22	<sup>5</sup> D <sub>3</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10312	4.8E-19	3.3E-21	4.8E-19	0.0E+00
23	<sup>5</sup> G <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-10125	2.4E-17	1.8E-20	6.0E-18	1.8E-17
24	<sup>5</sup> L <sub>10</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-9577	3.5E-20	3.5E-20	1.0E-23	0.0E+00
25	<sup>5</sup> G <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8781	1.4E-13	2.6E-17	3.5E-16	1.4E-13
26	<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8441	1.5E-16	1.1E-16	3.8E-17	0.0E+00
27	<sup>5</sup> G <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8261	4.2E-13	1.8E-16	3.9E-14	3.9E-13
28	<sup>5</sup> L <sub>9</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-8140	1.1E-15	1.1E-15	1.4E-17	0.0E+00
29	<sup>5</sup> L <sub>8</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-7358	1.5E-13	1.4E-13	3.1E-15	0.0E+00
30	<sup>5</sup> L <sub>7</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-7091	5.9E-12	2.2E-13	5.7E-12	0.0E+00
31	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-6878	2.1E-11	0.0E+00	0.0E+00	2.1E-11
32	<sup>5</sup> H <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-3657	4.3E-03	0.0E+00	0.0E+00	4.3E-03
33	<sup>5</sup> H <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2781	5.6E+00	0.0E+00	0.0E+00	5.6E+00
34	<sup>5</sup> H <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-2209	2.8E+02	0.0E+00	0.0E+00	2.8E+02
35	<sup>5</sup> F <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	-1614	2.6E+03	0.0E+00	0.0E+00	2.6E+03
36	<sup>5</sup> F <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.8	-1174	8.4E+04	0.0E+00	0.0E+00	8.4E+04
37	<sup>5</sup> I <sub>6</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	5.2	1050	5.2E+05	0.0E+00	0.0E+00	5.2E+05
38	<sup>5</sup> I <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	1060	7.5E+02	0.0E+00	0.0E+00	7.5E+02
39	<sup>5</sup> I <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.4	1438	4.0E+04	0.0E+00	0.0E+00	4.0E+04
40	<sup>5</sup> K <sub>5</sub> → <sup>7</sup> F <sub>5</sub>	S <sub>0</sub> →S <sub>1</sub>	0.0	4786	4.6E+03	0.0E+00	0.0E+00	4.6E+03
				$W_b^S$	1.0×10 <sup>7</sup>			
41	<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	S <sub>0</sub> →T <sub>1</sub>	0.0	-2346	7.4E-05	1.6E-07	7.3E-05	0.0E+00

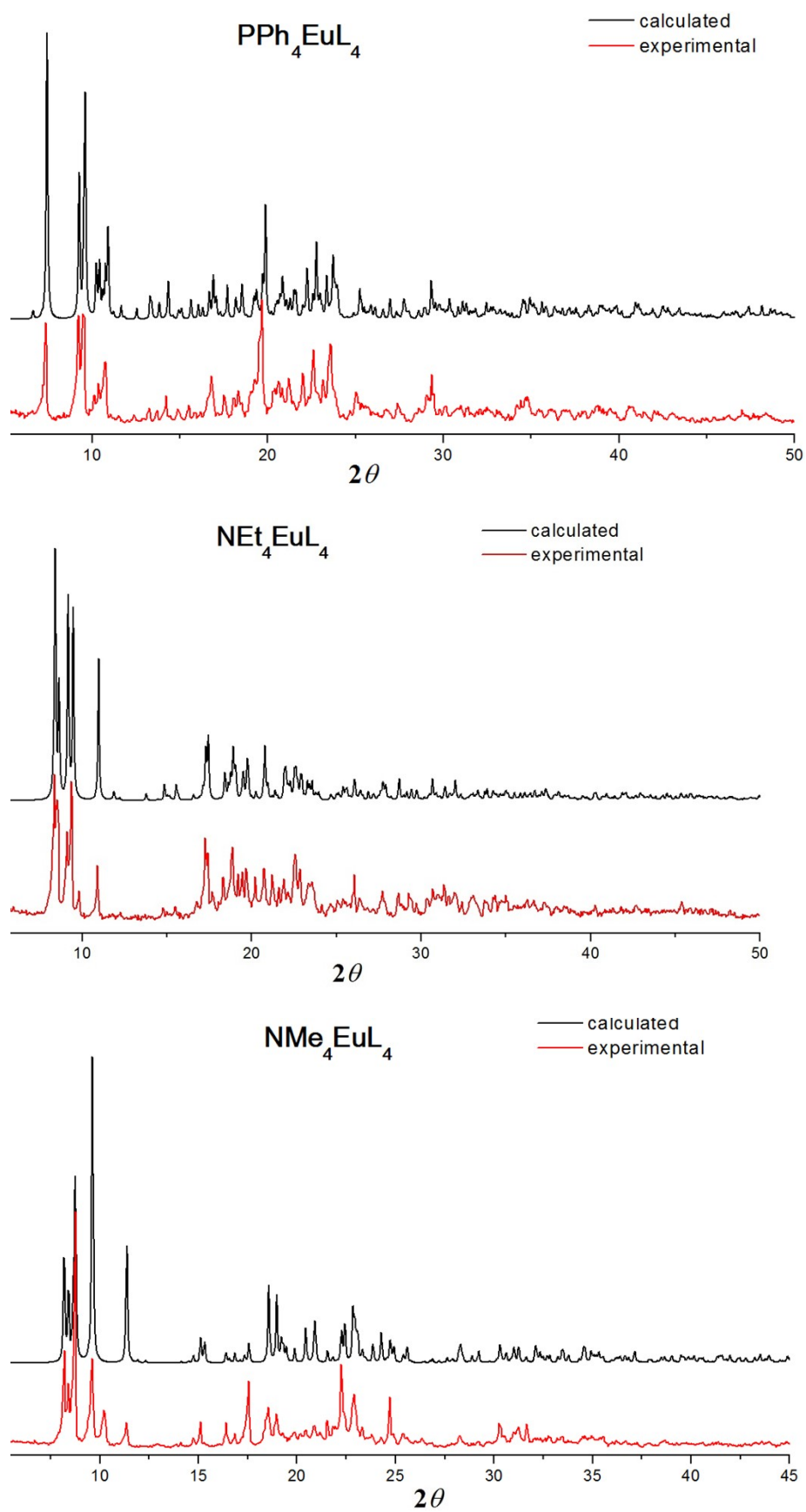


42	${}^5D_3 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	3446	1.3E-02	1.2E-02	3.9E-04	0.0E+00
43	${}^5G_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	45.4	3633	3.3E+06	5.0E-01	6.0E+00	3.3E+06
44	${}^5L_{10} \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	4181	1.4E-01	1.4E-01	2.0E-04	0.0E+00
45	${}^5G_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	2.7	4977	2.0E+05	5.1E-02	3.9E+00	2.0E+05
46	${}^5G_4 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	5497	3.7E-01	3.4E-02	3.4E-01	0.0E+00
47	${}^5L_9 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	5618	8.2E-02	8.1E-02	8.1E-04	0.0E+00
48	${}^5G_3 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6187	6.1E-03	5.9E-03	1.9E-04	0.0E+00
49	${}^5L_8 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6400	3.4E-02	3.4E-02	4.5E-05	0.0E+00
50	${}^5L_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	6667	1.7E+00	1.9E-02	8.2E-01	8.6E-01
51	${}^5L_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.3	6880	2.1E+04	0.0E+00	0.0E+00	2.1E+04
52	${}^5H_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.1	8589	9.7E+03	0.0E+00	0.0E+00	9.7E+03
53	${}^5H_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.6	10101	4.1E+04	0.0E+00	0.0E+00	4.1E+04
54	${}^5H_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	10977	3.2E-04	0.0E+00	0.0E+00	3.2E-04
55	${}^5F_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.4	12144	2.9E+04	0.0E+00	0.0E+00	2.9E+04
56	${}^5I_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	13799	2.8E+02	0.0E+00	0.0E+00	2.8E+02
57	${}^5I_6 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	14808	2.1E+03	0.0E+00	0.0E+00	2.1E+03
58	${}^5I_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	15196	1.5E+02	0.0E+00	0.0E+00	1.5E+02
59	${}^5K_5 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	18544	3.5E-01	0.0E+00	0.0E+00	3.5E-01
60	${}^5K_7 \rightarrow {}^7F_6$	$S_0 \rightarrow T_1$	0.0	18903	2.1E-08	0.0E+00	0.0E+00	2.1E-08
61	${}^5D_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	-4394	2.3E-04	1.2E-11	4.0E-08	2.3E-04
62	${}^5D_3 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	1398	4.8E+00	3.3E-02	4.8E+00	0.0E+00
63	${}^5G_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	8.0	1585	5.9E+05	6.3E-02	2.0E+01	5.9E+05
64	${}^5L_{10} \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	2133	5.0E-03	5.0E-03	1.4E-06	0.0E+00
65	${}^5G_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	26.7	2929	2.0E+06	3.8E-02	5.1E-01	2.0E+06
66	${}^5D_2 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	3269	3.1E-02	2.4E-02	7.6E-03	0.0E+00
67	${}^5G_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	3.8	3449	2.8E+05	1.4E-02	2.8E+00	2.8E+05
68	${}^5L_9 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	3570	4.2E-02	4.1E-02	5.0E-04	0.0E+00
69	${}^5L_8 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	4352	6.2E-02	6.1E-02	1.3E-03	0.0E+00
70	${}^5L_7 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	4619	5.4E-01	2.0E-02	5.2E-01	0.0E+00
71	${}^5L_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.1	4832	5.6E+03	0.0E+00	0.0E+00	5.6E+03
72	${}^5H_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.2	8053	1.5E+04	0.0E+00	0.0E+00	1.5E+04
73	${}^5H_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	2.0	8929	1.5E+05	0.0E+00	0.0E+00	1.5E+05
74	${}^5H_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	4.2	9501	3.1E+05	0.0E+00	0.0E+00	3.1E+05
75	${}^5F_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	1.4	10096	1.1E+05	0.0E+00	0.0E+00	1.1E+05
76	${}^5F_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	4.1	10536	3.0E+05	0.0E+00	0.0E+00	3.0E+05
77	${}^5I_6 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	12760	1.5E+03	0.0E+00	0.0E+00	1.5E+03
78	${}^5I_4 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	12770	2.2E+00	0.0E+00	0.0E+00	2.2E+00
79	${}^5I_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	13148	9.3E+01	0.0E+00	0.0E+00	9.3E+01
80	${}^5K_5 \rightarrow {}^7F_5$	$S_0 \rightarrow T_1$	0.0	16496	1.7E+00	0.0E+00	0.0E+00	1.7E+00
				$W_b^T$	$7.4 \times 10^6$			

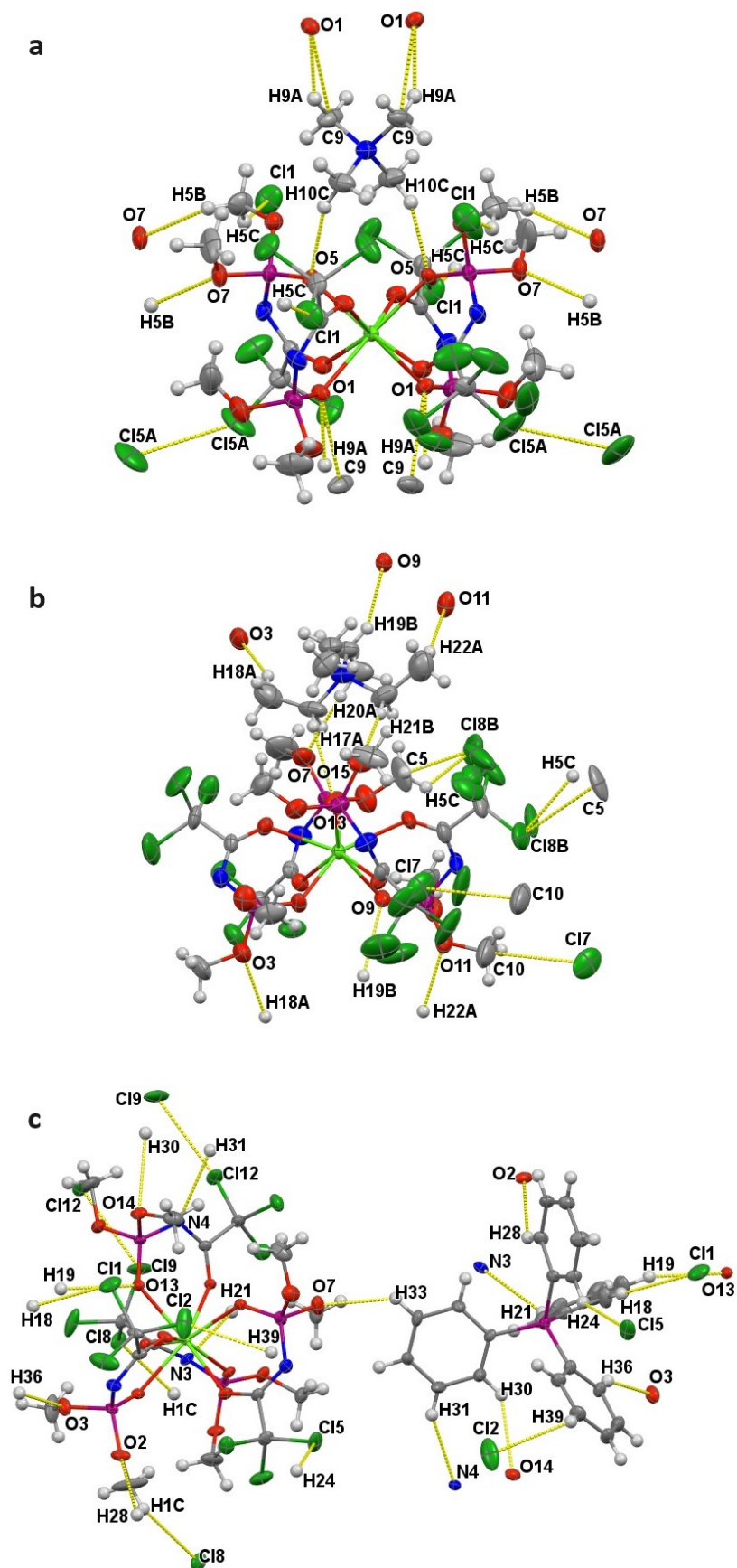
### 3. Figures



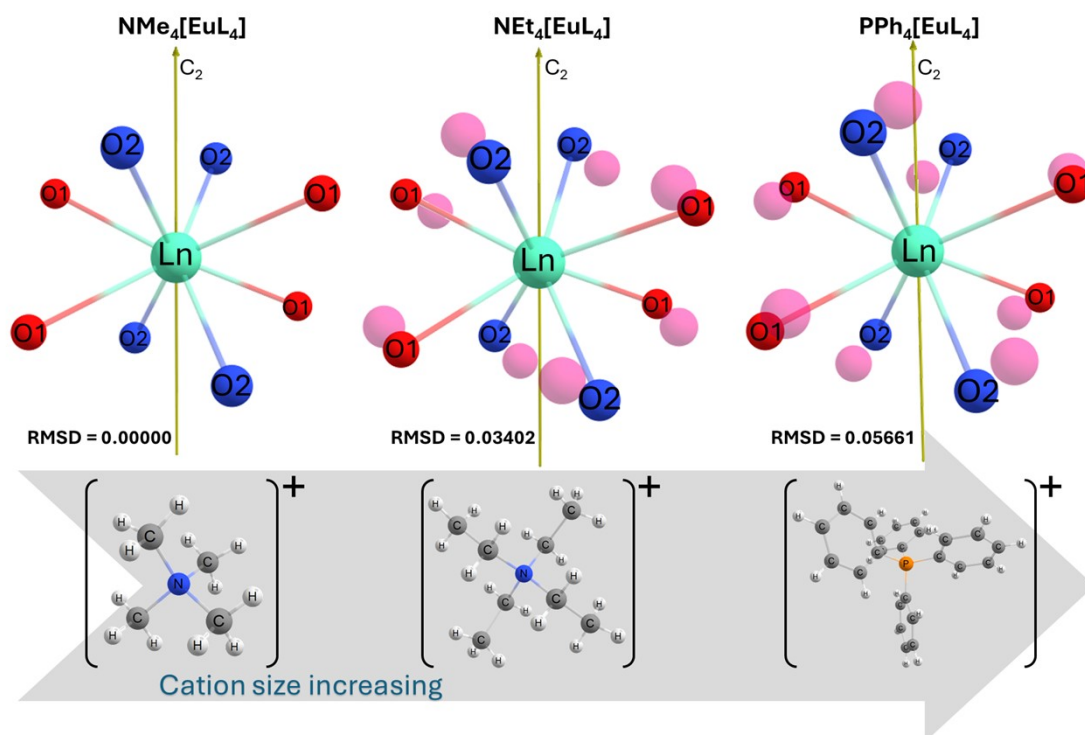
**Figure S1.** The crystal packing of  $\text{NMe}_4[\text{EuL}_4]$  (a),  $\text{NEt}_4[\text{EuL}_4]$  (b),  $\text{PPh}_4[\text{GdL}_4]$  (the cations are omitted) (c) viewed along the b-axis direction.



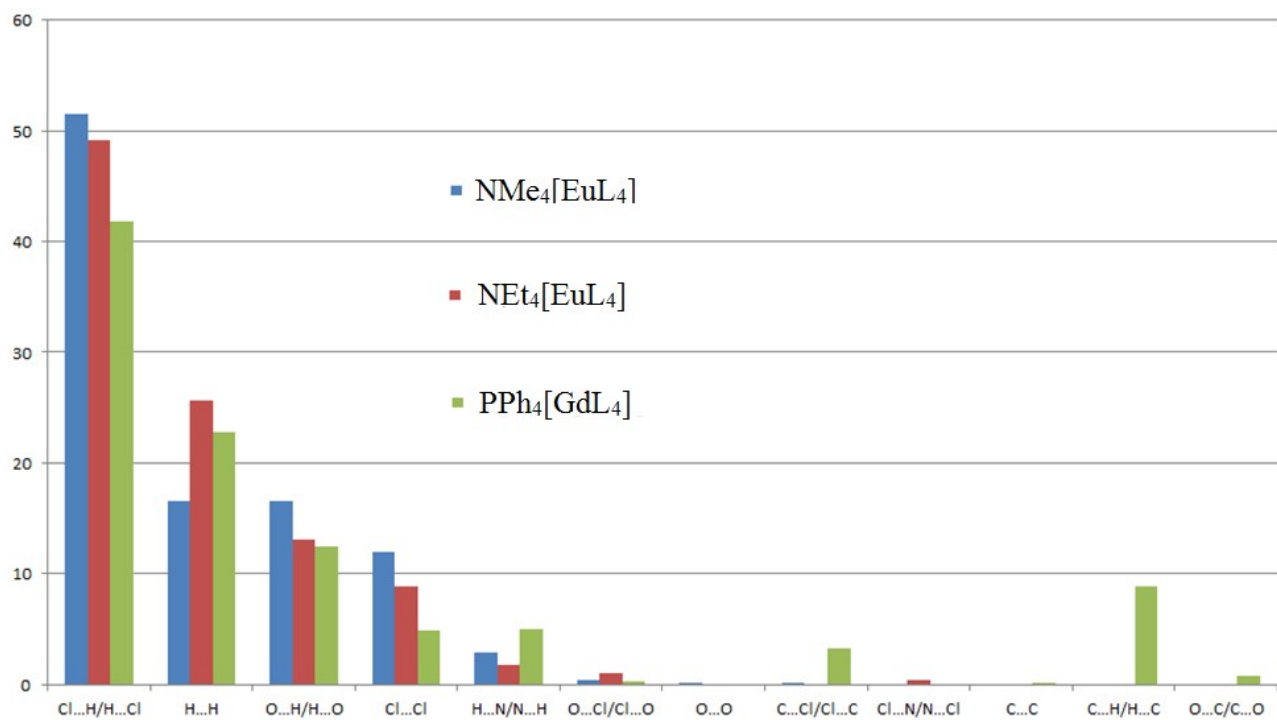
**Figure S2.** Calculated and experimental XRD patterns for the obtained europium complexes.



**Figure S3.** The inter- and intramolecular interactions in  $\text{NMe}_4[\text{EuL}_4]$  (a),  $\text{NET}_4[\text{EuL}_4]$  (b),  $\text{PPh}_4[\text{GdL}_4]$  (c).

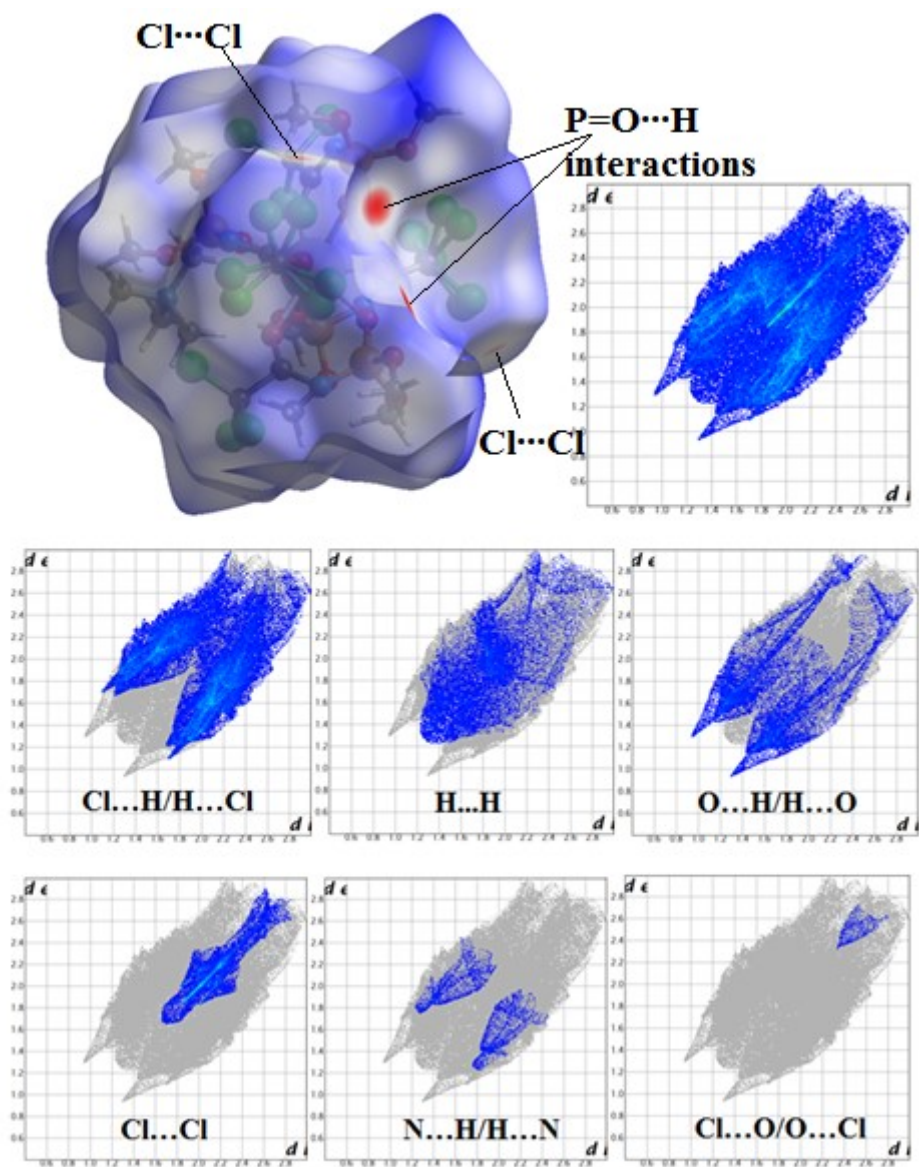


**Figure S4.** The effect of increasing cation size on the distortion of the coordination polyhedron of the studied compounds. The  $\text{NMe}_4[\text{EuL}_4]$  has an exact C<sub>2</sub> axis (RMSD = 0.00000), while the others deviate from the exact C<sub>2</sub> positions, represented by pink spheres. When the cation is changed to a larger one, the coordination polyhedron starts to distort, increasing the RMSD values, as illustrated. O1 stands for the oxygen atoms of the C=O groups, while O2 stands for the oxygen atoms of the P=O groups.

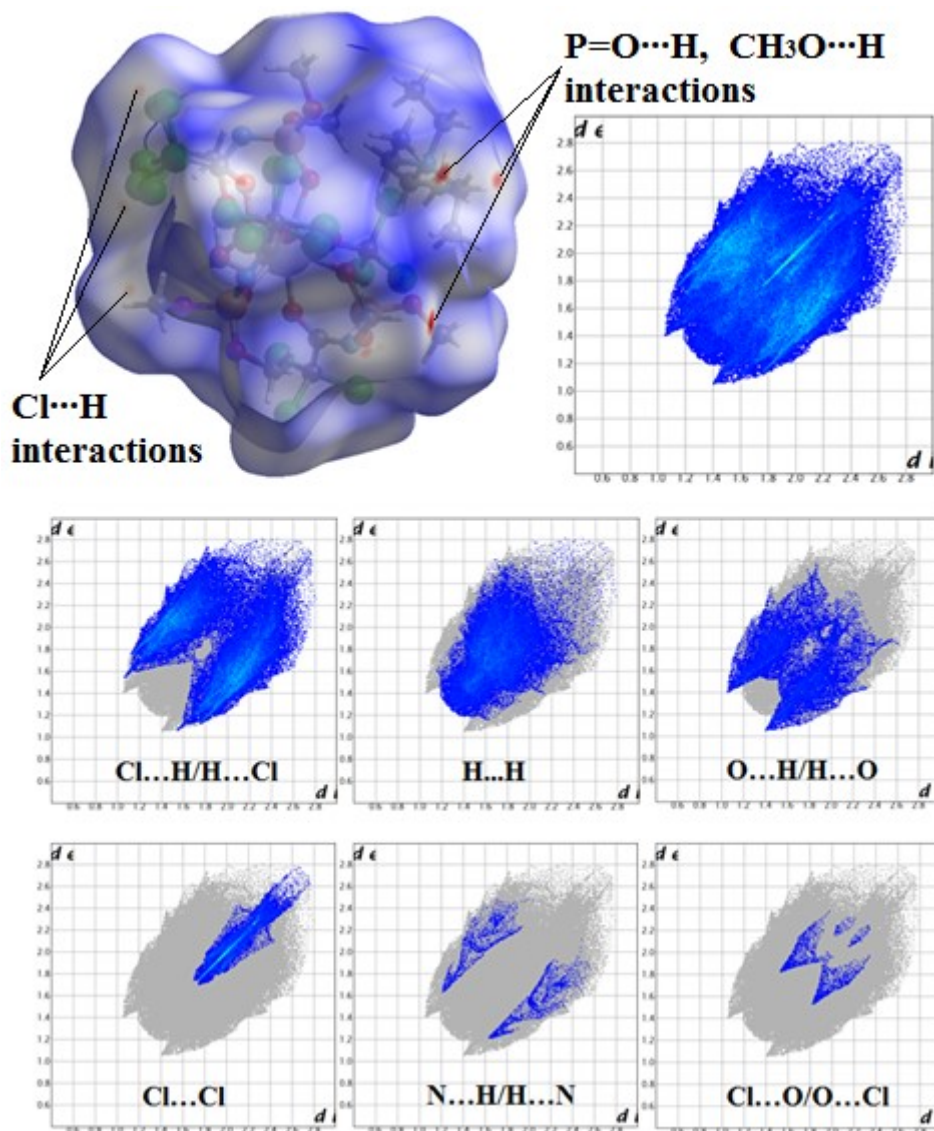


**Figure S5.** The relative contributions of various interactions into the total Hirshfeld surfaces for the obtained complexes (in %).



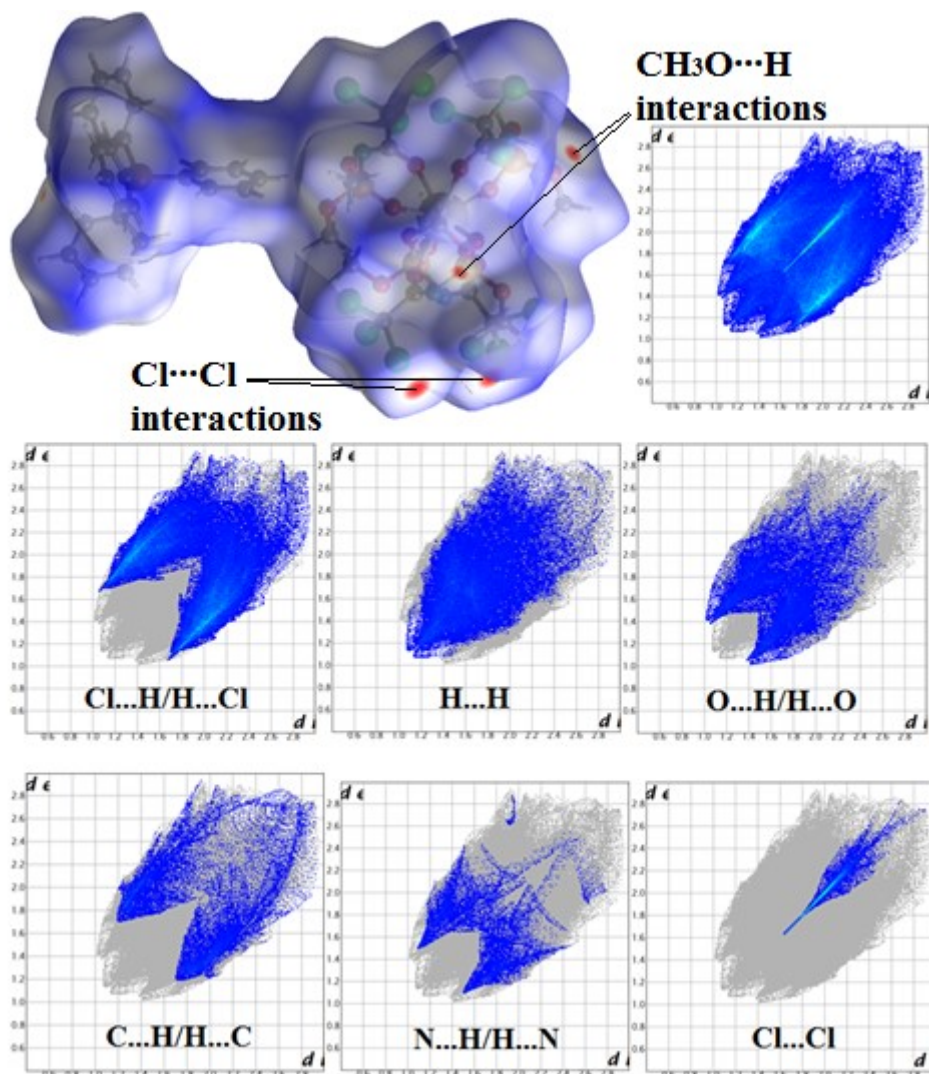


**Figure S6.** The Hirshfeld surface mapped over  $d_{\text{norm}}$  and two-dimensional fingerprint plots for the interactions with major contribution of  $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$  (51.5%),  $\text{H}\cdots\text{H}$  (16.5%),  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  (16.5%),  $\text{Cl}\cdots\text{Cl}$  (12.0%),  $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$  (2.9%), and  $\text{Cl}\cdots\text{O}/\text{O}\cdots\text{Cl}$  (0.4%) in  $\text{NMe}_4[\text{EuL}_4]$ .

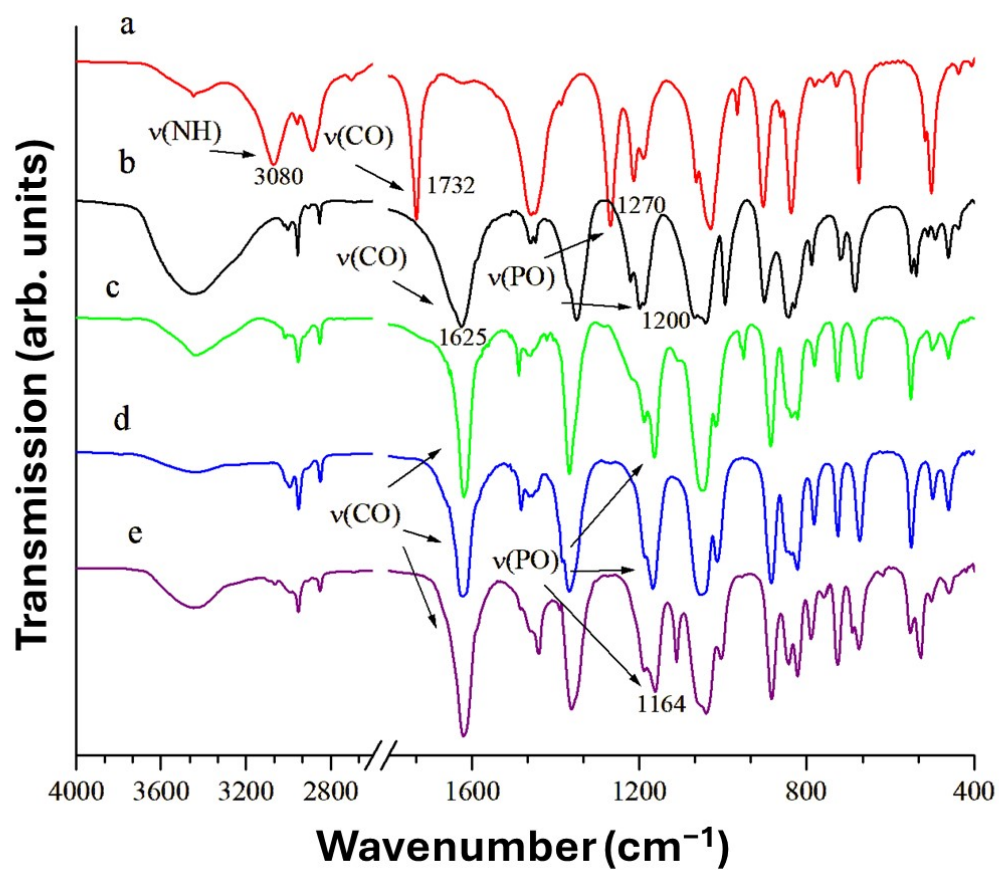


**Figure S7.** The Hirshfeld surface mapped over  $d_{\text{norm}}$  and two-dimensional fingerprint plots for the interactions with major contribution of Cl...H/H...Cl (49.1%), H...H (25.7%), O...H/H...O (13.1%), Cl...Cl (8.8%), H...N/N...H (1.7%), and Cl...O/O...Cl (1.0%) in NEt<sub>4</sub>[EuL<sub>4</sub>].





**Figure S8.** The Hirshfeld surface mapped over  $d_{\text{norm}}$  and two-dimensional fingerprint plots for the interactions with major contribution of Cl...H/H...Cl (41.8%), H...H (22.8%), O...H/H...O (12.5%), C...H/H...C (8.8%), H...N/N...H (5.0%), and Cl...Cl (4.9%) in PPh<sub>4</sub>[GdL<sub>4</sub>].



**Figure S9.** IR spectra for a) HL, b) NaL, c) NMe<sub>4</sub>[GdL<sub>4</sub>], d) NEt<sub>4</sub>[GdL<sub>4</sub>], and e) PPh<sub>4</sub>[GdL<sub>4</sub>].

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