

Electronic Supplementary Information (ESI)

**S-Heptazine N-Ligand Based Luminescent Coordination Materials: Synthesis,  
Structural and Luminescent Studies of Lanthanide-Cyamelurate Networks**

Mohamed Essalhi,<sup>a</sup> Midhun Mohan,<sup>a</sup> Gabriel Marineau-Plante,<sup>b</sup> Adrien Schlacter,<sup>b</sup>  
Thierry Maris,<sup>c</sup> Pierre D. Harvey\*<sup>b</sup> and Adam Duong\*<sup>a</sup>

<sup>a</sup> *Département de Chimie, Biochimie et physique, Institut de Recherche sur l'Hydrogène  
and Laboratory of Functional Materials for Energy and Nanotechnology (DuongLab),  
Université du Québec à Trois-Rivières, Trois-Rivières, Québec, G9A 5H7, Canada*

<sup>b</sup> *Département de chimie, Université de Sherbrooke, Sherbrooke, PQ, J1K 2R1, Canada*

<sup>c</sup> *Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada*

\*To whom correspondence should be addressed. E-mail: [adam.duong@uqtr.ca](mailto:adam.duong@uqtr.ca)

## Contents

**Figure S1.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Dy-Cy from Ln-Cy series 1. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Dy ion center in the crystal structure of Dy-Cy from Ln-Cy series 1..... 5

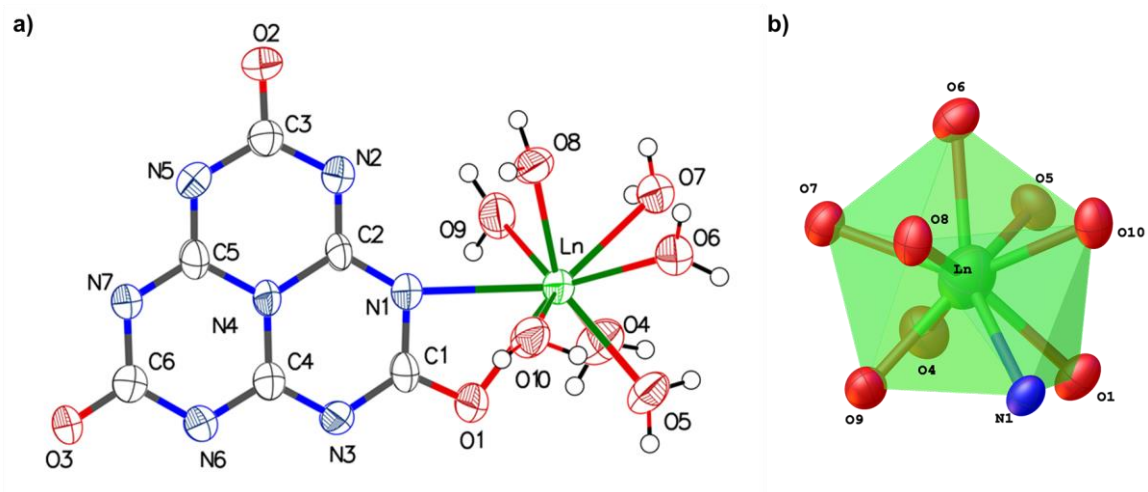
**Figure S2.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Ho-Cy from Ln-Cy series 2. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Ho ion center in the crystal structure of Ho-Cy from Ln-Cy series 2..... 6

**Figure S3.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Ln-Cy series 3 (Ln = Ce). The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b)

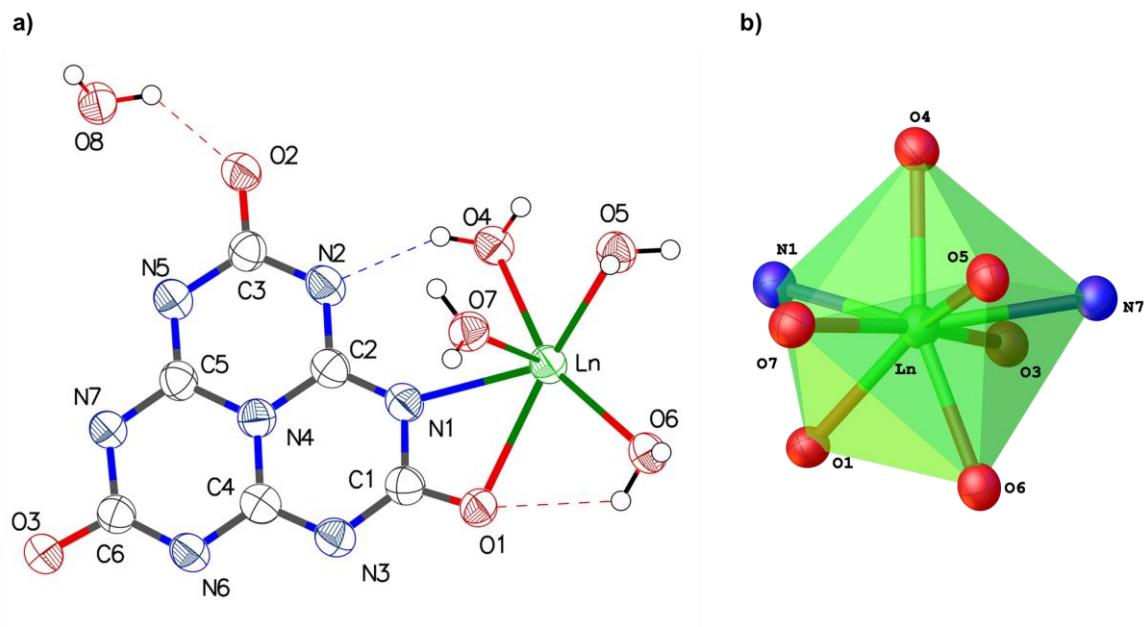
Coordination environment for Ln center in the crystal structure of Ln-Cy series 3 (Ln = Ce).....	7
<b>Figure S4.</b> a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of the Ln-Cy series 4 (Ln = La). The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Ln center in the crystal structure of Ln-Cy series 4 (Ln = La).....	8
<b>Table S1.</b> Crystal data and structure refinement for Ln-Cy (series 1).....	9
<b>Table S2.</b> Crystal data and structure refinement for Ln-Cy (series 2).....	10
<b>Table S3.</b> Crystal data and structure refinement for Ce-Cy (series 3).....	11
<b>Table S4.</b> Crystal data and structure refinement for La-Cy (series 4).....	12
<b>Table S5.</b> Effective ionic radii (Å) of Ln <sup>3+</sup> ions with corresponding coordination number (Shannon-Prewitt data).....	12
<b>Figure S5.</b> Effective ionic radius (Å) vs Ln <sup>3+</sup> ions (cn = coordination number).....	13
<b>Figure S6.</b> Two-dimensional fingerprint plots of the Ln-Cy series 1.....	14
<b>Figure S7.</b> Two-dimensional fingerprint plots of Ln-Cy series 2.....	14
<b>Figure S8.</b> Two-dimensional fingerprint plots of Ln-Cy series 3.....	15
<b>Figure S9.</b> Two-dimensional fingerprint plots of Ln-Cy series 4.....	15
<b>Figure S10.</b> FTIR spectra of Ln-Cy series 1 in comparison with potassium cyamelurate.....	16
<b>Figure S11.</b> FTIR spectra of Ln-Cy series 2 in comparison with potassium cyamelurate.....	16
<b>Figure S12.</b> FTIR spectra of Ln-Cy series 3 in comparison with potassium cyamelurate.....	17
<b>Figure S13.</b> FTIR spectra of Ln-Cy series 4 in comparison with potassium cyamelurate.....	17
<b>Figure S14.</b> Experimental and simulated PXRD patterns for La-Cy compound.....	18

<b>Figure S15.</b> Experimental and simulated PXRD patterns for Ce-Cy compound.....	18
<b>Figure S16.</b> Experimental and simulated PXRD patterns for Ln-Cy series 1. ....	19
<b>Figure S17.</b> Experimental and simulated PXRD patterns for Ln-Cy series 2. ....	19
<b>Figure S18.</b> Thermogravimetric analysis curves for Ln-Cy series 1. ....	20
<b>Figure S19.</b> Thermogravimetric analysis curves for Ln-Cy series 2. ....	20
<b>Figure S20.</b> Thermogravimetric analysis curve for Ln-Cy series 3.....	21
<b>Figure S21.</b> Thermogravimetric analysis curve for Ln-Cy series 4.....	21
<b>Figure S22.</b> Absorption (black), emission (red) and excitation (blue) spectra for K <sub>3</sub> Cy in solution in water at 298 K ( $\lambda_{\text{ex}} = 270$ nm, $\lambda_{\text{em}} = 364$ nm). The weak signal at ~305 nm is suspected to be fluorescence, and the large and intense one centered at 364 nm is assigned to a triplet emission. Unfortunately, the ligand decomposes upon laser exposure at 266 nm, so the fluorescence lifetime is not accessible. ....	22
<b>Figure S23.</b> Side and front view of geometry optimization for Cy <sup>3-</sup> anion in the gas phase. ....	22
<b>Table S6.</b> Cartesian coordinates (Å) of the geometry optimized Cy <sup>3-</sup> in the gas phase. ..	23
<b>Table S7.</b> Calculated position, oscillator strength (f) and major contributions (%) of the first 100 singlet-singlet electronic transitions for Cy <sup>3-</sup> in the gas phase. ....	23
<b>Figure S24.</b> Simulated absorption spectrum for Cy <sup>3-</sup> in the gas phase by TDDFT computations. Bar graph reporting the calculated oscillator strength and the calculated position of the 100th electronic transitions calculated by TDDFT for Cy <sup>3-</sup> in the gas phase (bar graph; f = computed oscillator strength). ....	27
<b>Figure S25.</b> Solid-state absorption (black), emission (red) and excitation (blue) spectra for La-Cy at 298 K ( $\lambda_{\text{ex}} = 270$ nm, $\lambda_{\text{em}} = 335$ nm) and 77K ( $\lambda_{\text{ex}} = 270$ nm, $\lambda_{\text{em}} = 355$ nm). ....	28
<b>Figure S26.</b> Decay of emission intensity, fit, IRF and residual of Gd-Cy at 298 K. $\lambda = 339$ nm ( $\lambda_{\text{ex}} = 277$ nm), $\tau_e$ {f%} = 15 $\mu$ s {100}, $\chi^2 = 1.070$ .....	28
<b>Figure S27.</b> Solid-state absorption (black), emission (red) and excitation (blue) spectra for Sm-Cy at 77K ( $\lambda_{\text{ex}} = 290$ nm, $\lambda_{\text{em}} = 643$ nm).....	29

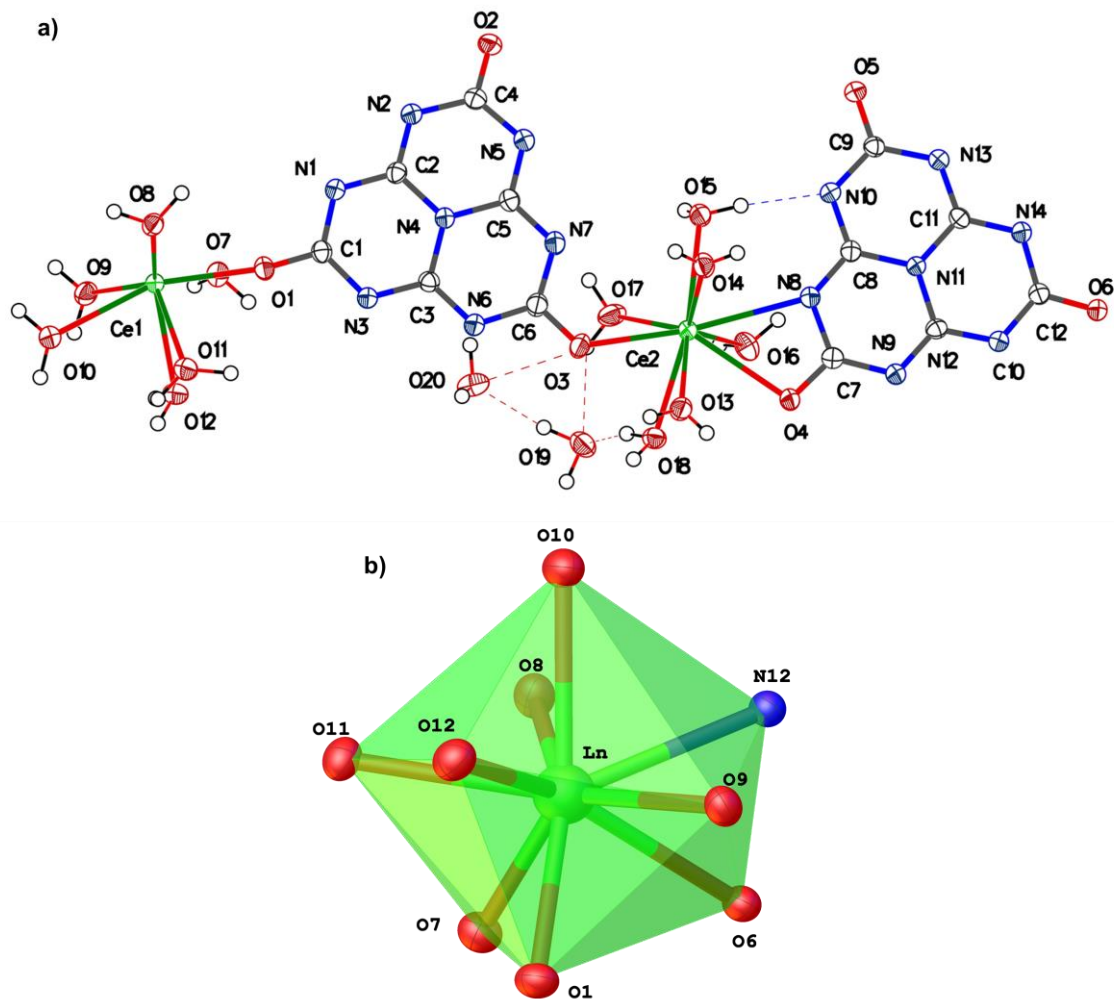
<b>Figure S28.</b> Solid-state absorption (black), emission (red) and excitation (blue) spectra for Eu-Cy at 77K ( $\lambda_{\text{ex}} = 300$ nm, $\lambda_{\text{em}} = 615$ nm). .....	29
<b>Figure S29.</b> Decay of emission intensity, fit, IRF and residual of Eu-Cy. Left at 77 K $\lambda = 615$ nm ( $\lambda_{\text{ex}} = 300$ nm), $\tau_e$ {f%} = 16 $\mu\text{s}$ {100}, $\chi^2 = 1.001$ .....	30
<b>Figure S31.</b> Decay of emission intensity, fit, IRF and residual of Tb-Cy. Left, at 77 K $\lambda = 620$ nm ( $\lambda_{\text{ex}} = 270$ nm), $\tau_e$ {f%} = 50 $\mu\text{s}$ {100}, $\chi^2 = 1.031$ .....	31
<b>Figure S32.</b> Solid-state absorption (black), emission (red) and excitation (blue) spectra for Dy-Cy at 298 K ( $\lambda_{\text{ex}} = 270$ nm, $\lambda_{\text{em}} = 571$ nm) and 77K ( $\lambda_{\text{ex}} = 270$ nm, $\lambda_{\text{em}} = 575$ nm). .....	31
<b>Figure S33.</b> Decay of emission intensity, fit, IRF and residual of Dy-Cy at 298 K. $\lambda = 570$ nm ( $\lambda_{\text{ex}} = 270$ nm), $\tau_e$ {f%} = 3.48 $\mu\text{s}$ {100}, $\chi^2 = 1.034$ .....	32
<b>Figure S34.</b> Solid-state absorption (black), emission (red) and excitation (blue) spectra for Er-Cy at 298 K ( $\lambda_{\text{ex}} = 300$ nm, $\lambda_{\text{em}} = 336$ nm). .....	32
<b>Figure S35.</b> Solid-state absorption (black) spectra for Ce-Cy at 298 K. ....	33
<b>Figure S36.</b> Solid-state absorption (black) spectra for Pr-Cy- at 298 K.....	33
<b>Figure S37.</b> Solid-state absorption (black) for Ho-Cy at 298 K. ....	34
<b>Table S8.</b> Photophysical properties of all emissive Ln-Cy.....	34



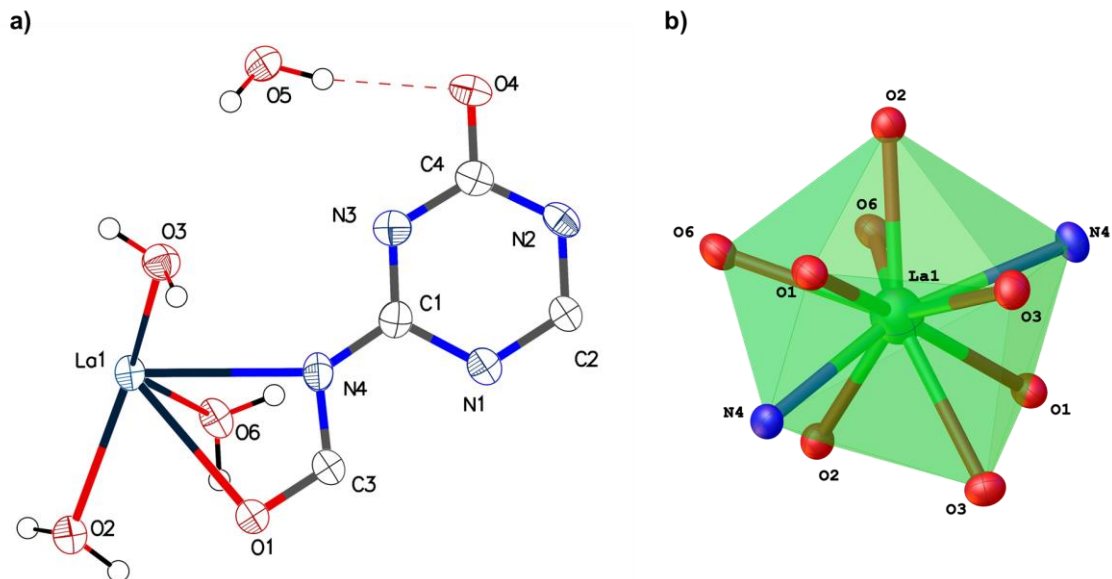
**Figure S1.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Dy-Cy from Ln-Cy series 1. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Dy ion center in the crystal structure of Dy-Cy from Ln-Cy series 1.



**Figure S2.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Ho-Cy from Ln-Cy series 2. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Ho ion center in the crystal structure of Ho-Cy from Ln-Cy series 2.



**Figure S3.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of Ln-Cy series 3 (Ln = Ce). The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Ln center in the crystal structure of Ln-Cy series 3 (Ln = Ce).



**Figure S4.** a) Thermal atomic displacement ellipsoid plot of the asymmetric unit of the Ln-Cy series 4 (Ln = La). The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size. b) Coordination environment for Ln center in the crystal structure of Ln-Cy series 4 (Ln = La).



**Table S1.** Crystal data and structure refinement for Ln-Cy (series 1).

Identification code	Sm-Cy	Eu-Cy	Tb-Cy	Dy-Cy
<b>Empirical formula</b>	C <sub>6</sub> H <sub>14</sub> N <sub>7</sub> O <sub>10</sub> Sm	C <sub>6</sub> H <sub>14</sub> N <sub>7</sub> O <sub>10</sub> Eu	C <sub>6</sub> H <sub>14</sub> N <sub>7</sub> O <sub>10</sub> Tb	C <sub>6</sub> H <sub>14</sub> N <sub>7</sub> O <sub>10</sub> Dy
<b>CCDC number</b>	2178361	2178362	2178359	2178360
<b>Formula weight</b>	494.59	496.20	503.16	506.74
<b>Temperature/K</b>	298	295	298	295
<b>Crystal system</b>	monoclinic	monoclinic	monoclinic	monoclinic
<b>Space group</b>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<b>a/Å</b>	11.9028(6)	11.8872(6)	11.8582(4)	11.8401(11)
<b>b/Å</b>	6.8680(3)	6.8605(3)	6.8416(2)	6.8183(7)
<b>c/Å</b>	16.7913(8)	16.7718(8)	16.6967(5)	16.6650(16)
<b>α/°</b>	90	90	90	90
<b>β/°</b>	93.617(2)	93.608(2)	93.700(1)	93.753(4)
<b>γ/°</b>	90	90	90	90
<b>Volume/Å<sup>3</sup></b>	1369.93(11)	1365.07(11)	1351.76(7)	1342.5(2)
<b>Z</b>	4	4	4	<b>2 4</b>
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	2.398	2.414	2.472	2.507
<b>μ/mm<sup>-1</sup></b>	32.936	33.639	26.484	30.541
<b>F(000)</b>	964.0	968.0	976.0	980.0
<b>Radiation</b>	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
<b>2θ range for data collection/°</b>	8.848 to 140.184	8.86 to 141.39	8.882 to 140.274	8.892 to 140.642
<b>Reflections collected</b>	35375	23809	24483	18994
<b>Independent reflections</b>	2614 [R <sub>int</sub> = 0.0372, R <sub>sigma</sub> = 0.0135]	2598 [R <sub>int</sub> = 0.0440, R <sub>sigma</sub> = 0.0222]	2561 [R <sub>int</sub> = 0.0402, R <sub>sigma</sub> = 0.0213]	2503 [R <sub>int</sub> = 0.0752, R <sub>sigma</sub> = 0.0442]
<b>Goodness-of-fit on F<sup>2</sup></b>	1.036	1.043	1.053	1.108
<b>Final R indexes [I ≥ 2σ(I)]</b>	R <sub>1</sub> = 0.0206, wR <sub>2</sub> = 0.0571	R <sub>1</sub> = 0.0331, wR <sub>2</sub> = 0.0769	R <sub>1</sub> = 0.0248, wR <sub>2</sub> = 0.0616	R <sub>1</sub> = 0.0714, wR <sub>2</sub> = 0.1944
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0207, wR <sub>2</sub> = 0.0571	R <sub>1</sub> = 0.0339, wR <sub>2</sub> = 0.0774	R <sub>1</sub> = 0.0265, wR <sub>2</sub> = 0.0626	R <sub>1</sub> = 0.0787, wR <sub>2</sub> = 0.2056

**Table S2.** Crystal data and structure refinement for Ln-Cy (series 2).

Identification code	Ho-Cy	Er-Cy	Yb-Cy
<b>Empirical formula</b>	C <sub>6</sub> H <sub>10</sub> N <sub>7</sub> O <sub>8</sub> Ho	C <sub>6</sub> H <sub>10</sub> N <sub>7</sub> O <sub>8</sub> Er	C <sub>6</sub> H <sub>10</sub> N <sub>7</sub> O <sub>8</sub> Yb
<b>CCDC number</b>	2178364	2178356	2178363
<b>Formula weight</b>	946.28	475.47	481.25
<b>Temperature/K</b>	298	100	100
<b>Crystal system</b>	monoclinic	monoclinic	monoclinic
<b>Space group</b>	Cc	Cc	Cc
<b>a/Å</b>	5.7138(3)	5.69360(10)	5.6782(2)
<b>b/Å</b>	12.1155(7)	12.0266(3)	12.0332(4)
<b>c/Å</b>	17.6748(10)	17.6197(4)	17.5540(6)
<b>α/°</b>	90	90	90
<b>β/°</b>	91.136(2)	90.8670(10)	90.652(2)
<b>γ/°</b>	90	90	90
<b>Volume/Å<sup>3</sup></b>	1223.31(12)	1206.36(5)	1199.33(7)
<b>Z</b>	4	4	4
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	2.569	2.618	2.665
<b>μ/mm<sup>-1</sup></b>	12.716	13.558	15.071
<b>F(000)</b>	904.0	908.0	916.0
<b>Radiation</b>	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
<b>2θ range for data collection/°</b>	10.01 to 140.308	10.042 to 143.402	10.078 to 143.992
<b>Reflections collected</b>	11086	14549	20269
<b>Independent reflections</b>	2228	2115	2318
	[R <sub>int</sub> = 0.0486, R <sub>sigma</sub> = 0.0272]	[R <sub>int</sub> = 0.0186, R <sub>sigma</sub> = 0.0116]	[R <sub>int</sub> = 0.0274, R <sub>sigma</sub> = 0.0145]
<b>Goodness-of-fit on F<sup>2</sup></b>	1.078	1.106	1.079
<b>Final R indexes [I&gt;2σ (I)]</b>	R <sub>1</sub> = 0.0411, wR <sub>2</sub> = 0.0984	R <sub>1</sub> = 0.0246, wR <sub>2</sub> = 0.0635	R <sub>1</sub> = 0.0207, wR <sub>2</sub> = 0.0518
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0415, wR <sub>2</sub> = 0.0990	R <sub>1</sub> = 0.0246, wR <sub>2</sub> = 0.0635	R <sub>1</sub> = 0.0209, wR <sub>2</sub> = 0.0519

**Table S3.** Crystal data and structure refinement for Ce-Cy (series 3).

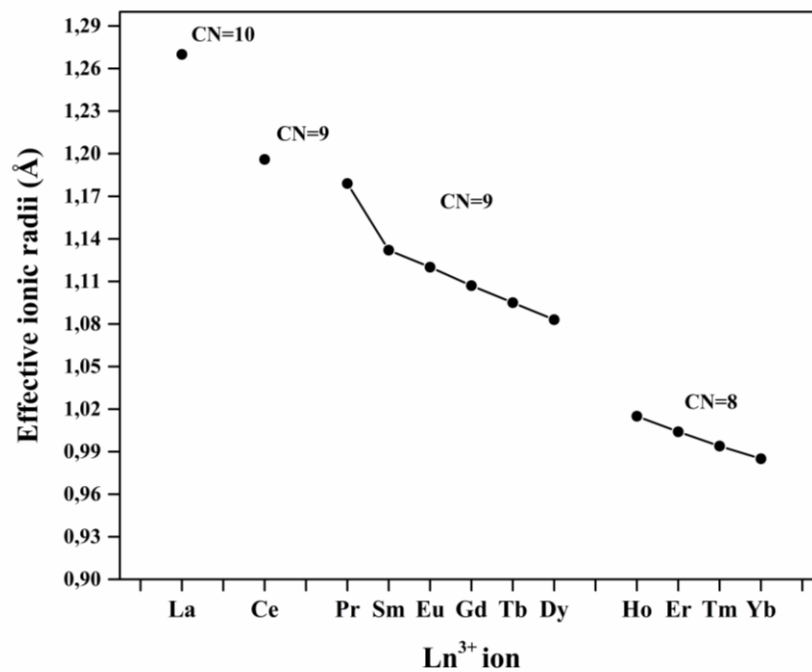
<b>Identification code</b>	<b>Ce-Cy</b>
<b>Empirical formula</b>	C <sub>6</sub> H <sub>14</sub> CeN <sub>7</sub> O <sub>10</sub>
<b>CCDC number</b>	2178358
<b>Formula weight</b>	484.36
<b>Temperature/K</b>	150
<b>Crystal system</b>	monoclinic
<b>Space group</b>	P2 <sub>1</sub> /c
<b>a/Å</b>	6.6711(4)
<b>b/Å</b>	19.7592(12)
<b>c/Å</b>	21.1063(13)
<b>α/°</b>	90
<b>β/°</b>	98.303(2)
<b>γ/°</b>	90
<b>Volume/Å<sup>3</sup></b>	2753.0(3)
<b>Z</b>	8
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	2.337
<b>μ/mm<sup>-1</sup></b>	18.091
<b>F(000)</b>	1896.0
<b>Radiation</b>	GaKα (λ = 1.34139)
<b>2θ range for data collection/°</b>	5.356 to 121.44
<b>Index ranges</b>	-8 ≤ h ≤ 8, -25 ≤ k ≤ 25, -27 ≤ l ≤ 27
<b>Reflections collected</b>	79204
<b>Independent reflections</b>	6336 [R <sub>int</sub> = 0.0309, R <sub>sigma</sub> = 0.0125]
<b>Data/restraints/parameters</b>	6336/0/448
<b>Goodness-of-fit on F<sup>2</sup></b>	1.081
<b>Final R indexes [I ≥ 2σ (I)]</b>	R <sub>1</sub> = 0.0188, wR <sub>2</sub> = 0.0502
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0195, wR <sub>2</sub> = 0.0506

**Table S4.** Crystal data and structure refinement for La-Cy (series 4).

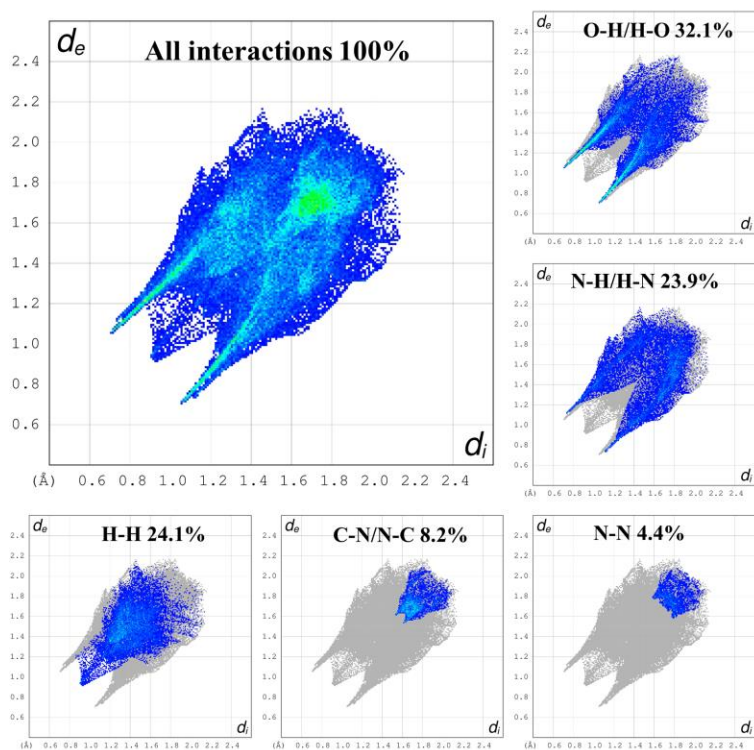
<b>Identification code</b>	<b>La-Cy</b>
<b>Empirical formula</b>	C <sub>6</sub> H <sub>14</sub> LaN <sub>7</sub> O <sub>10</sub>
<b>CCDC number</b>	2178357
<b>Formula weight</b>	483.15
<b>Temperature/K</b>	100
<b>Crystal system</b>	orthorhombic
<b>Space group</b>	I2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<b>a/Å</b>	6.5379(2)
<b>b/Å</b>	10.6082(3)
<b>c/Å</b>	19.3914(6)
<b>α/°</b>	90
<b>β/°</b>	90
<b>γ/°</b>	90
<b>Volume/Å<sup>3</sup></b>	1344.90(7)
<b>Z</b>	4
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	2.386
<b>μ/mm<sup>-1</sup></b>	17.378
<b>F(000)</b>	944.0
<b>Radiation</b>	GaKα (λ = 1.34139)
<b>2θ range for data collection/°</b>	7.934 to 109.854
<b>Reflections collected</b>	11301
<b>Independent reflections</b>	1269 [R <sub>int</sub> = 0.0309, R <sub>sigma</sub> = 0.0157]
<b>Goodness-of-fit on F<sup>2</sup></b>	1.095
<b>Final R indexes [I ≥ 2σ (I)]</b>	R <sub>1</sub> = 0.0403, wR <sub>2</sub> = 0.0992
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0403, wR <sub>2</sub> = 0.0993

**Table S5.** Effective ionic radii (Å) of Ln<sup>3+</sup> ions with corresponding coordination number (Shannon-Prewitt data).

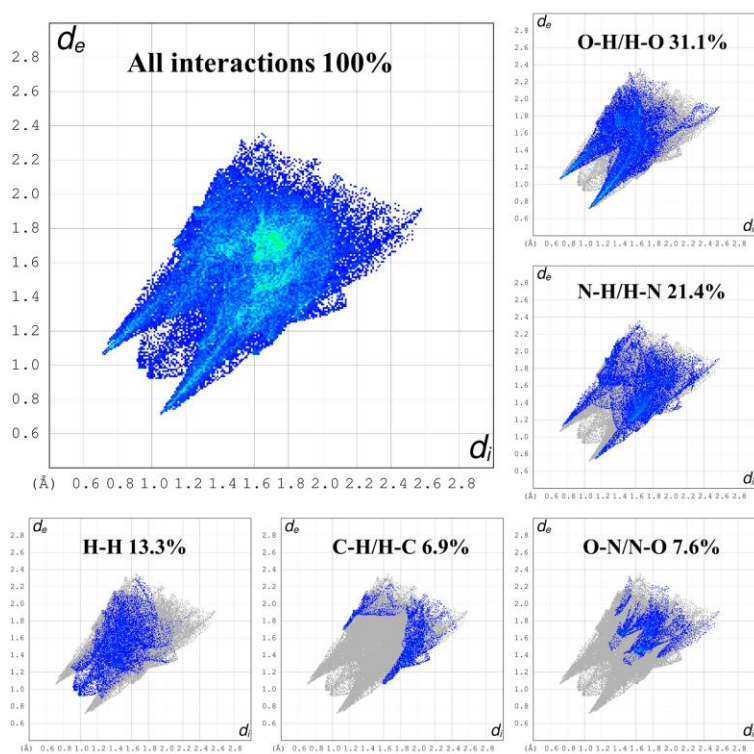
Ln-Cy series	Ln ion	Effective ionic radii (Å)	Charge density (C.mm <sup>-3</sup> )	Coordination number (CN)
3	La <sup>3+</sup>	1.270	72	10
4	Ce <sup>3+</sup>	1.196	75	9
1	Pr <sup>3+</sup>	1.179	79	9
	Sm <sup>3+</sup>	1.132	86	
	Eu <sup>3+</sup>	1.120	88	
	Gd <sup>3+</sup>	1.107	91	
	Tb <sup>3+</sup>	1.095	96	
	Dy <sup>3+</sup>	1.083	99	
2	Ho <sup>3+</sup>	1.015	102	8
	Er <sup>3+</sup>	1.004	105	
	Tm <sup>3+</sup>	0.994	108	
	Yb <sup>3+</sup>	0.985	111	



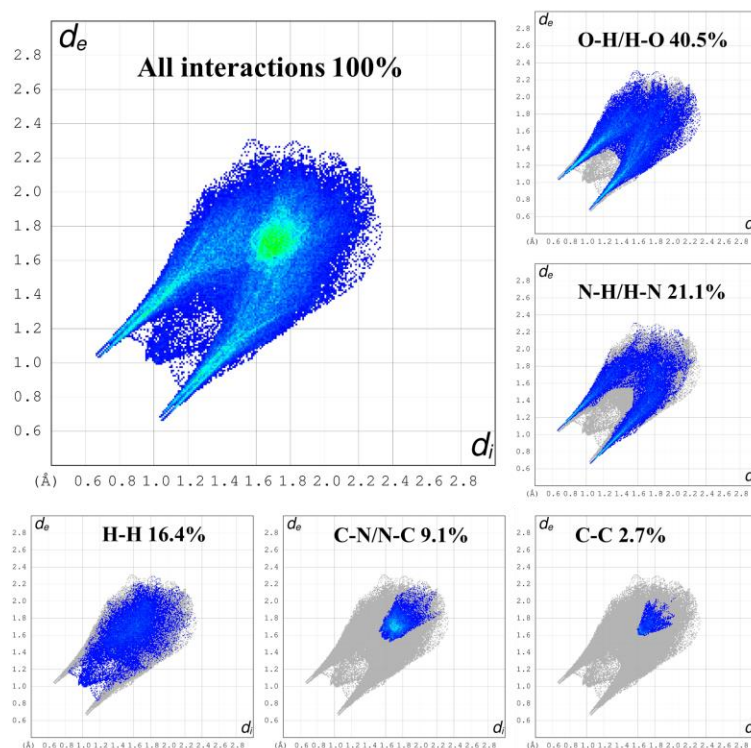
**Figure S5.** Effective ionic radius (Å) vs Ln<sup>3+</sup> ions (cn = coordination number).



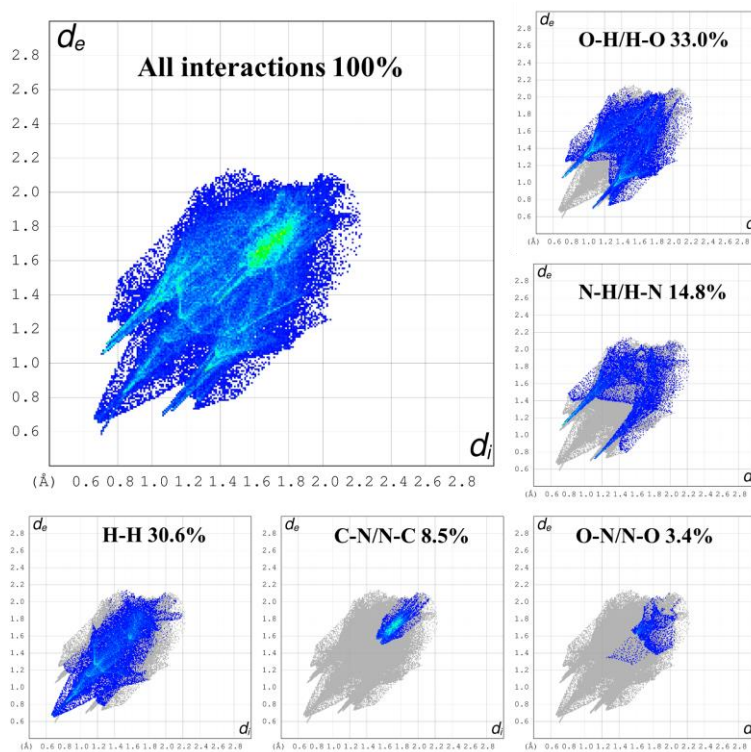
**Figure S6.** Two-dimensional fingerprint plots of the Ln-Cy series 1.



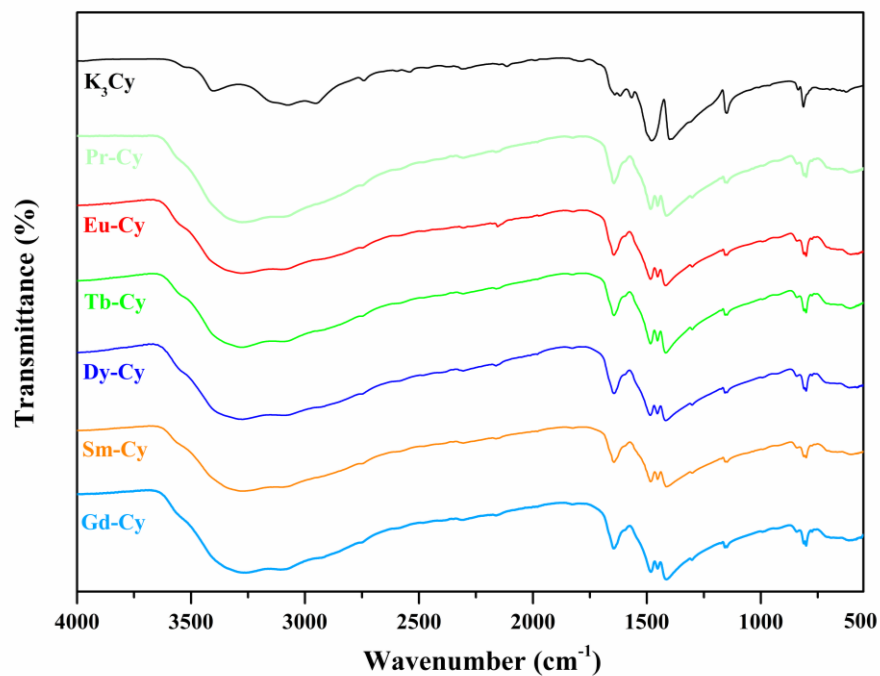
**Figure S7.** Two-dimensional fingerprint plots of Ln-Cy series 2.



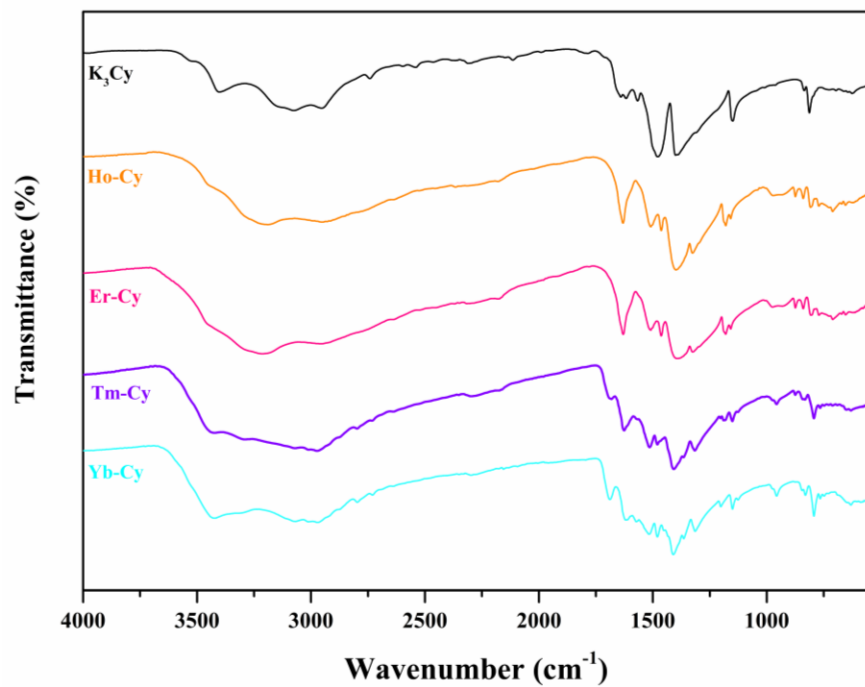
**Figure S8.** Two-dimensional fingerprint plots of Ln-Cy series 3.



**Figure S9.** Two-dimensional fingerprint plots of Ln-Cy series 4.

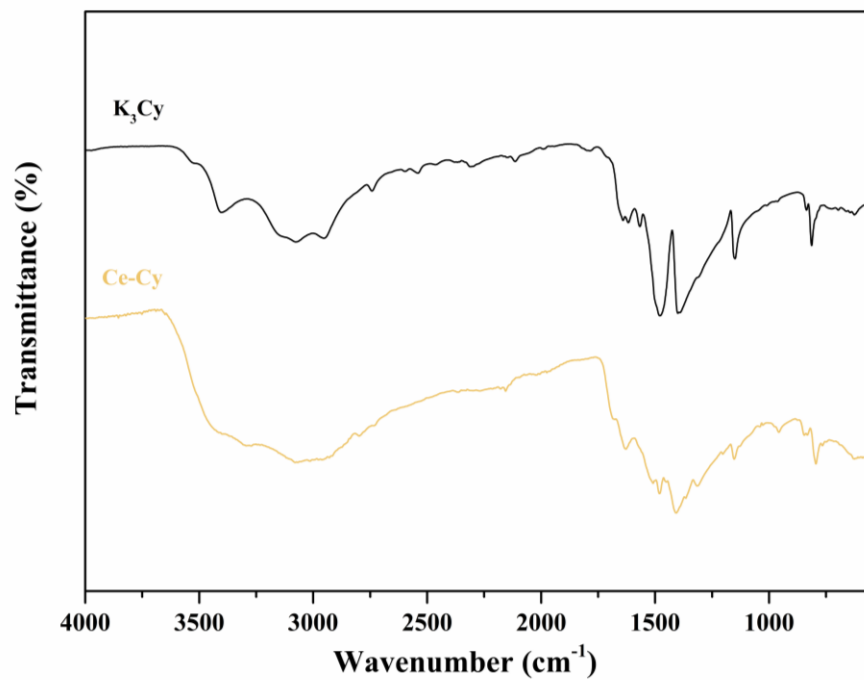


**Figure S10.** FTIR spectra of Ln-Cy series 1 in comparison with potassium cyamelurate.

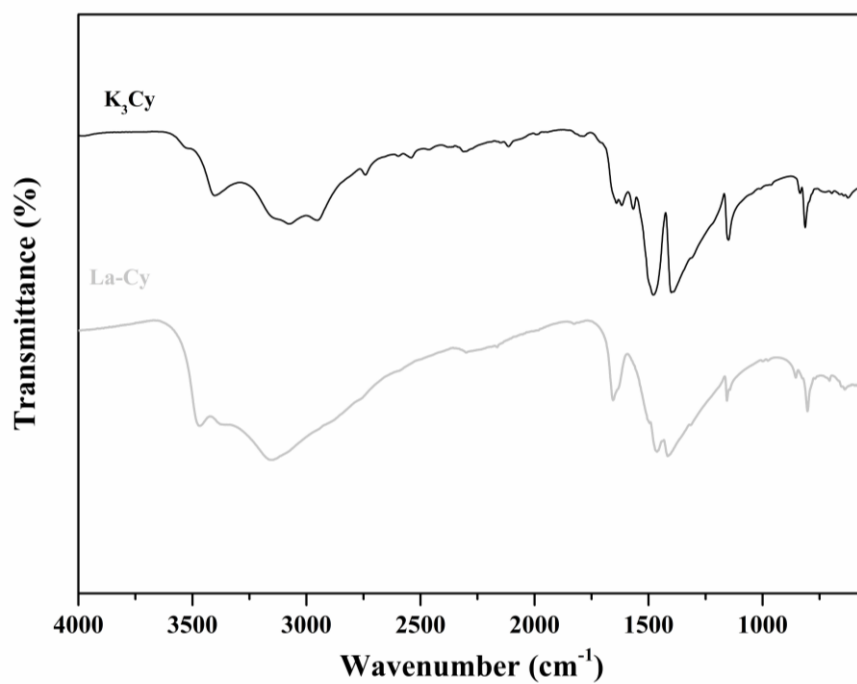


**Figure S11.** FTIR spectra of Ln-Cy series 2 in comparison with potassium cyamelurate.

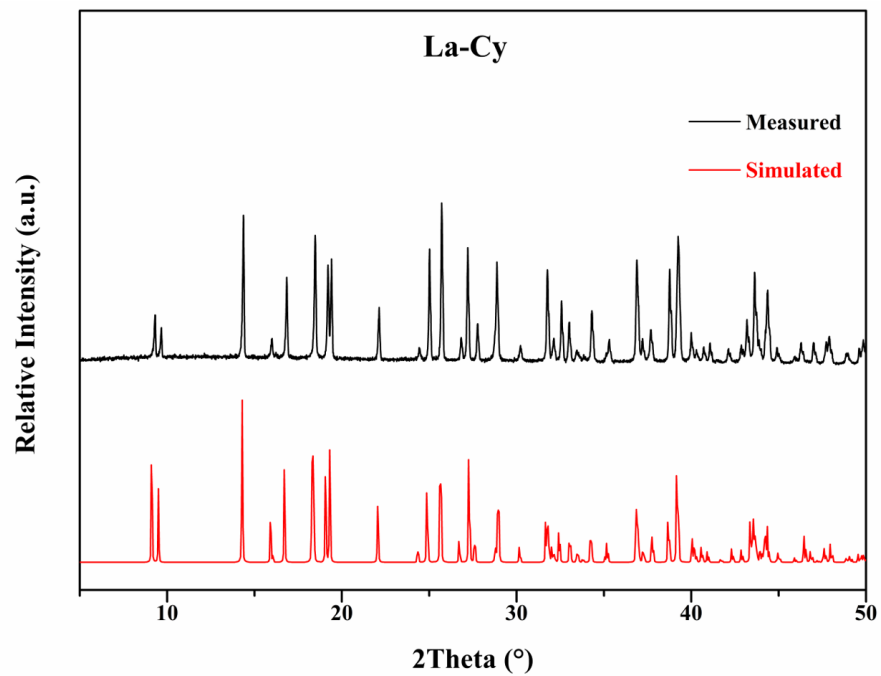




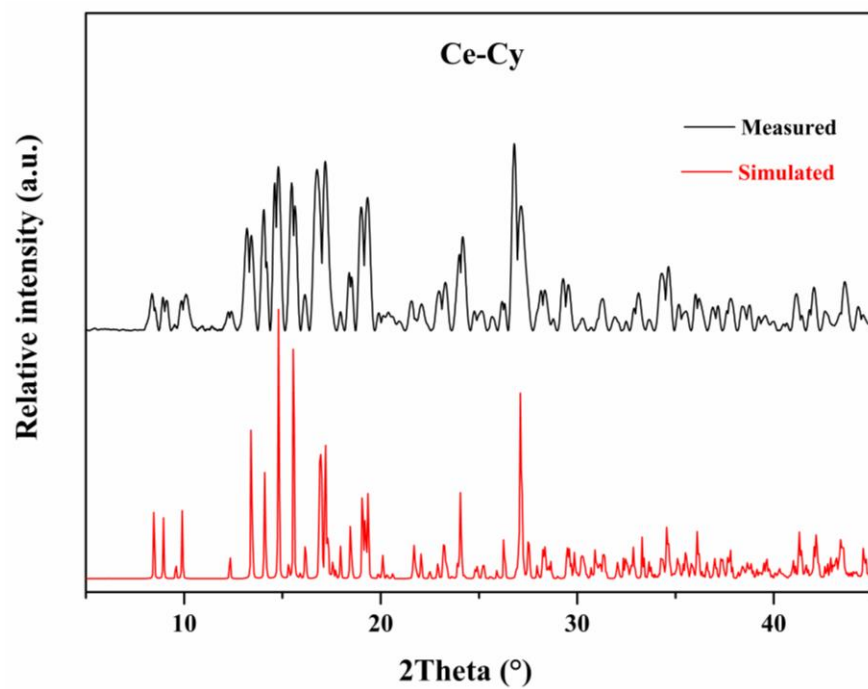
**Figure S12.** FTIR spectra of Ln-Cy series 3 in comparison with potassium cyamelurate.



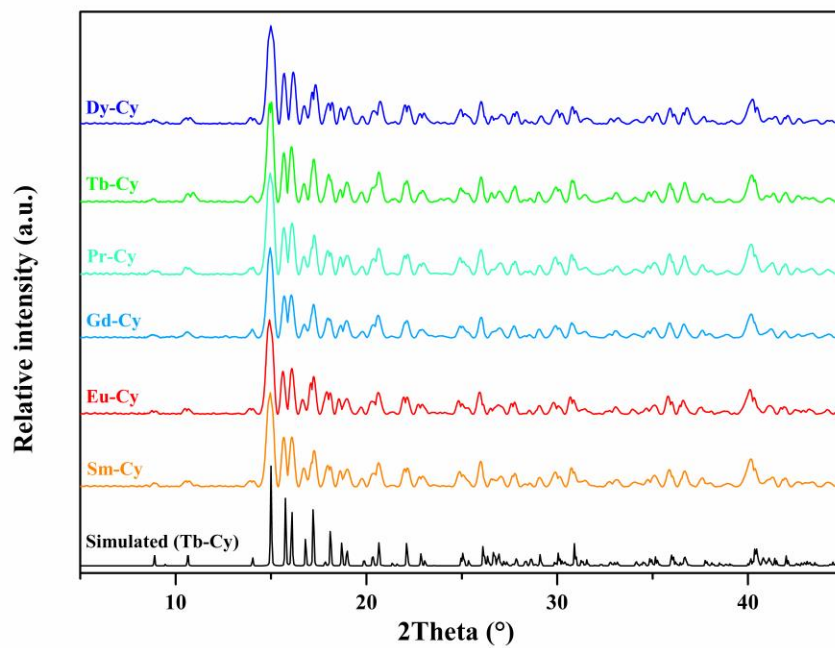
**Figure S13.** FTIR spectra of Ln-Cy series 4 in comparison with potassium cyamelurate.



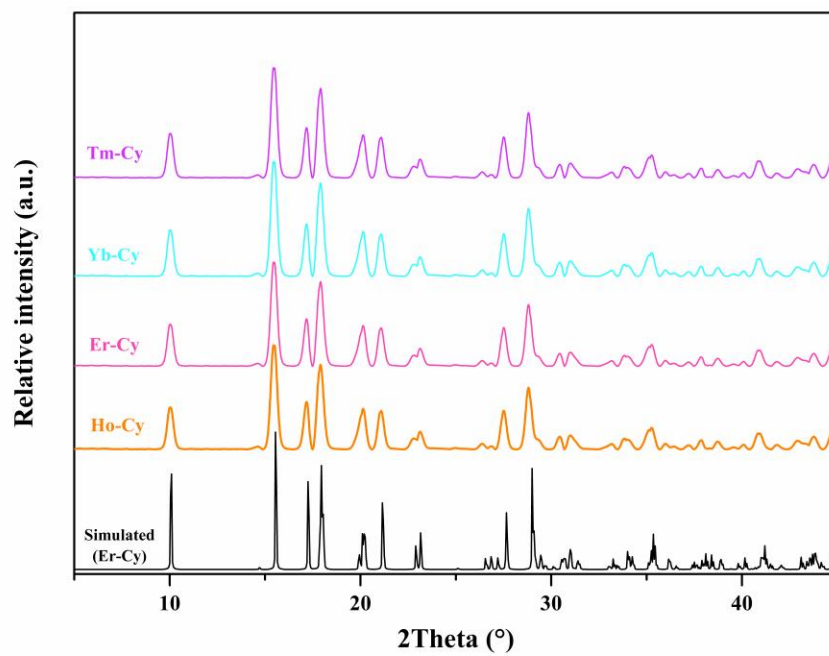
**Figure S14.** Experimental and simulated PXRD patterns for La-Cy compound.



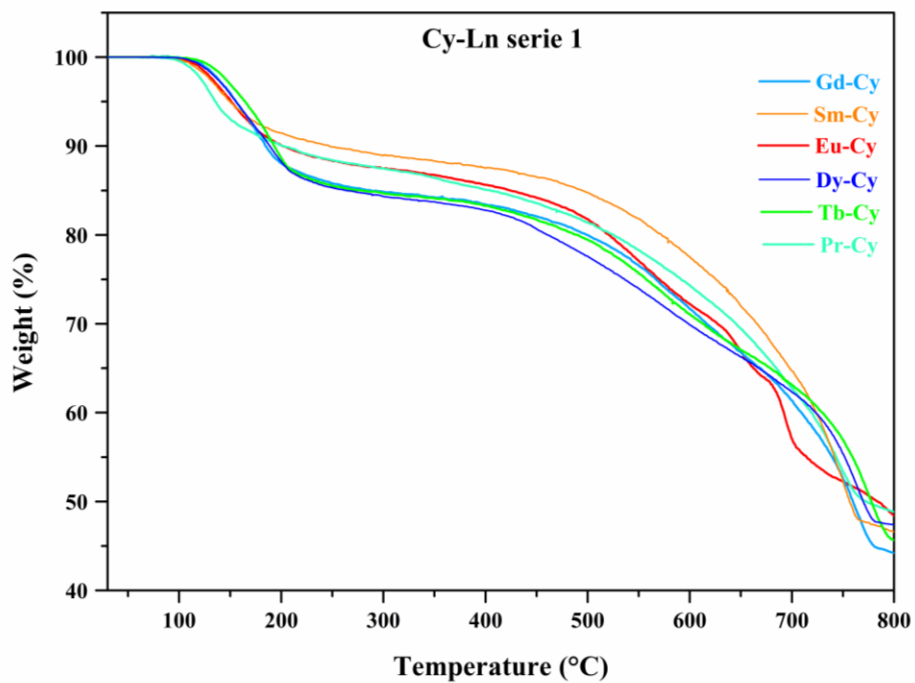
**Figure S15.** Experimental and simulated PXRD patterns for Ce-Cy compound.



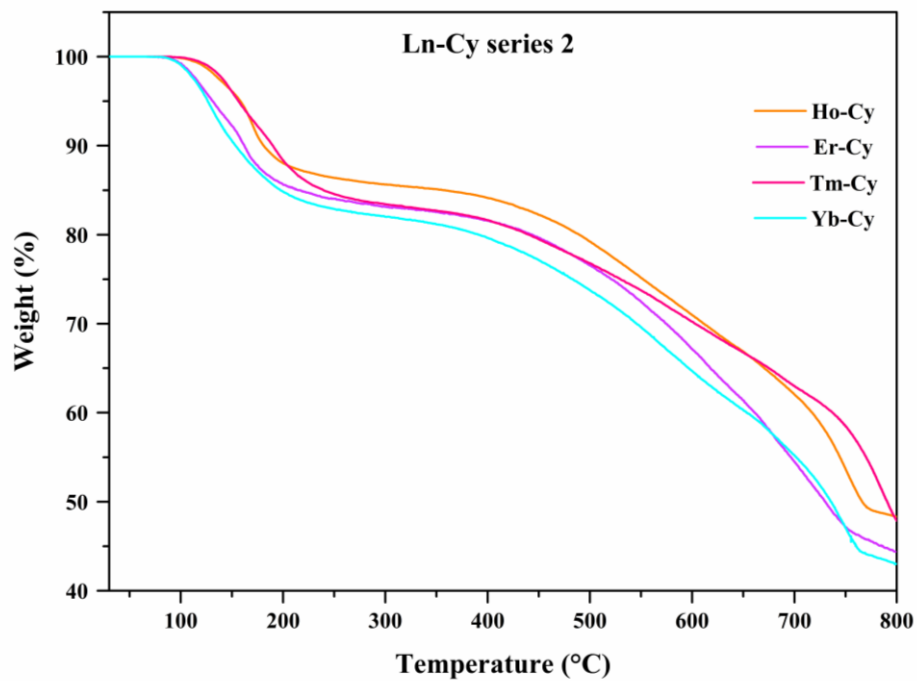
**Figure S16.** Experimental and simulated PXRD patterns for Ln-Cy series 1.



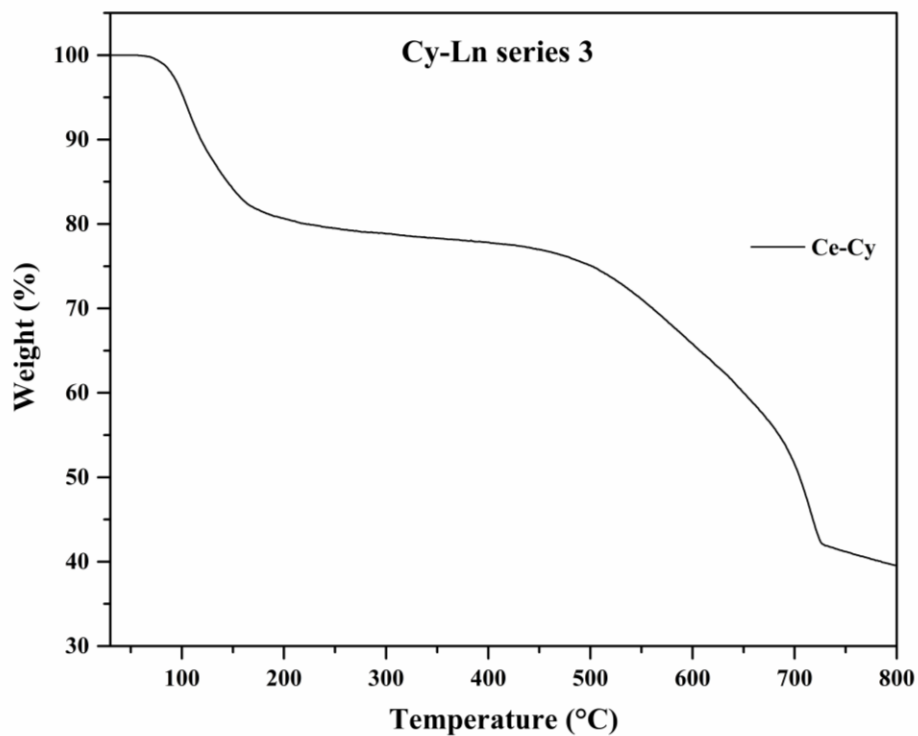
**Figure S17.** Experimental and simulated PXRD patterns for Ln-Cy series 2.



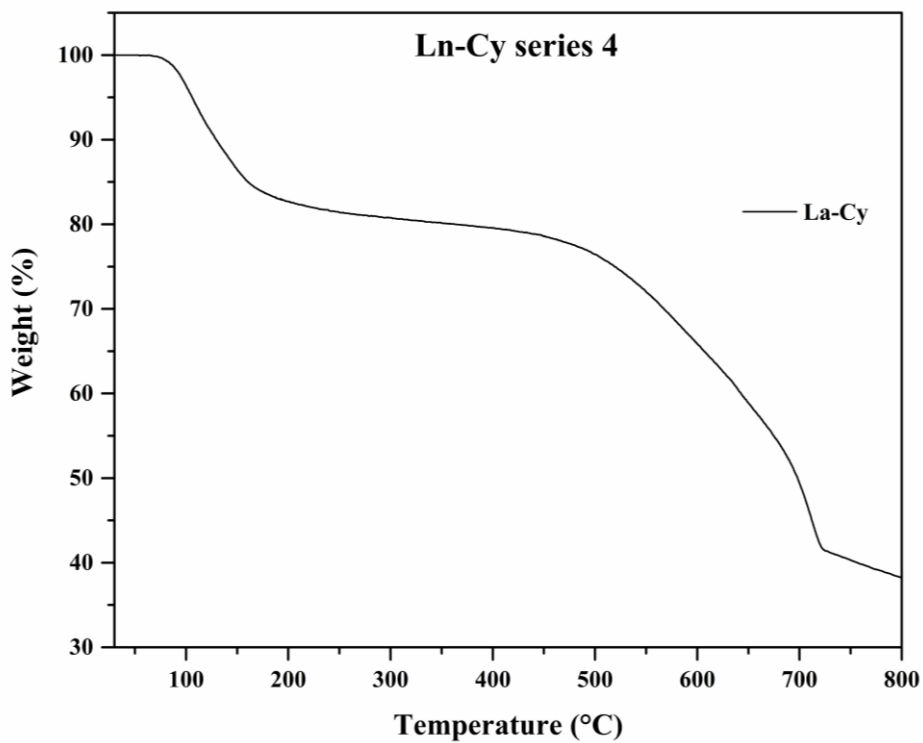
**Figure S18.** Thermogravimetric analysis curves for Ln-Cy series 1.



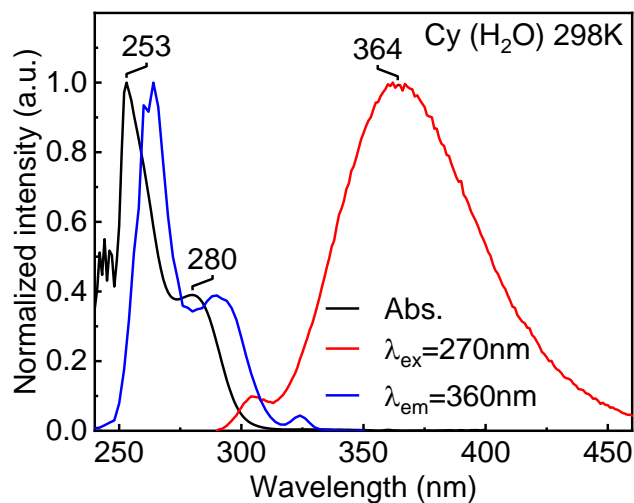
**Figure S19.** Thermogravimetric analysis curves for Ln-Cy series 2.



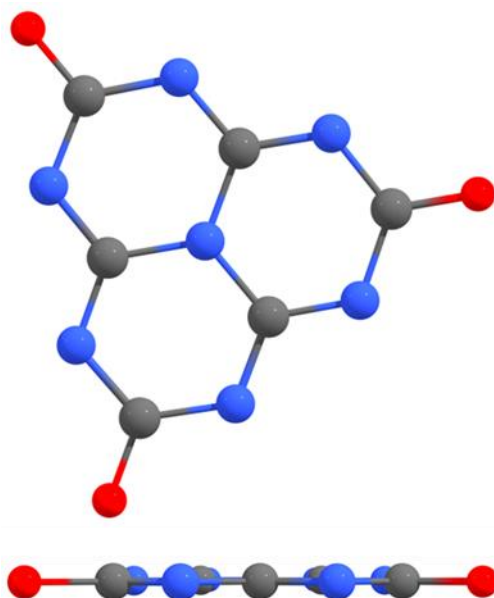
**Figure S20.** Thermogravimetric analysis curve for Ln-Cy series 3.



**Figure S21.** Thermogravimetric analysis curve for Ln-Cy series 4.



**Figure S22.** Absorption (black), emission (red) and excitation (blue) spectra for  $\text{K}_3\text{Cy}$  in solution in water at 298 K ( $\lambda_{\text{ex}} = 270 \text{ nm}$ ,  $\lambda_{\text{em}} = 364 \text{ nm}$ ). The weak signal at  $\sim 305 \text{ nm}$  is suspected to be fluorescence, and the large and intense one centered at 364 nm is assigned to a triplet emission. Unfortunately, the ligand decomposes upon laser exposure at 266 nm, so the fluorescence lifetime is not accessible.



**Figure S23.** Side and front view of geometry optimization for  $\text{Cy}^{3-}$  anion in the gas phase.

**Table S6.** Cartesian coordinates (Å) of the geometry optimized  $\text{Cy}^{3-}$  in the gas phase.

Atoms	X	Y	Z
N	-0.616832047104	4.593426455720	10.643241677131
N	-2.392938011823	4.179950631859	12.175222354486
N	-2.601393328827	5.897099191815	10.457273921951
N	-0.850536754913	6.277494976359	8.975304675126
N	1.194261540371	4.960235032302	9.140301135928
N	1.392707332124	3.321883430688	10.778282948480
N	-0.443605631222	2.922080382750	12.331305935801
O	1.503605907509	1.736624383553	12.415036752309
O	-4.268256069265	5.459625132085	11.951980835584
O	0.914746741299	6.585211070393	7.563679330435
C	-1.164439084449	3.881151730106	11.743329421367
C	-3.110839886592	5.184571683521	11.536714492874
C	-1.374686841214	5.614201193252	10.009908851508
C	0.429182880429	5.953775768550	8.540049561437
C	0.688544242850	4.284265570210	10.175829308703
C	0.831078298913	2.641808627374	11.852851066965

**Table S7.** Calculated position, oscillator strength (f) and major contributions (%) of the first 100 singlet-singlet electronic transitions for  $\text{Cy}^{3-}$  in the gas phase.

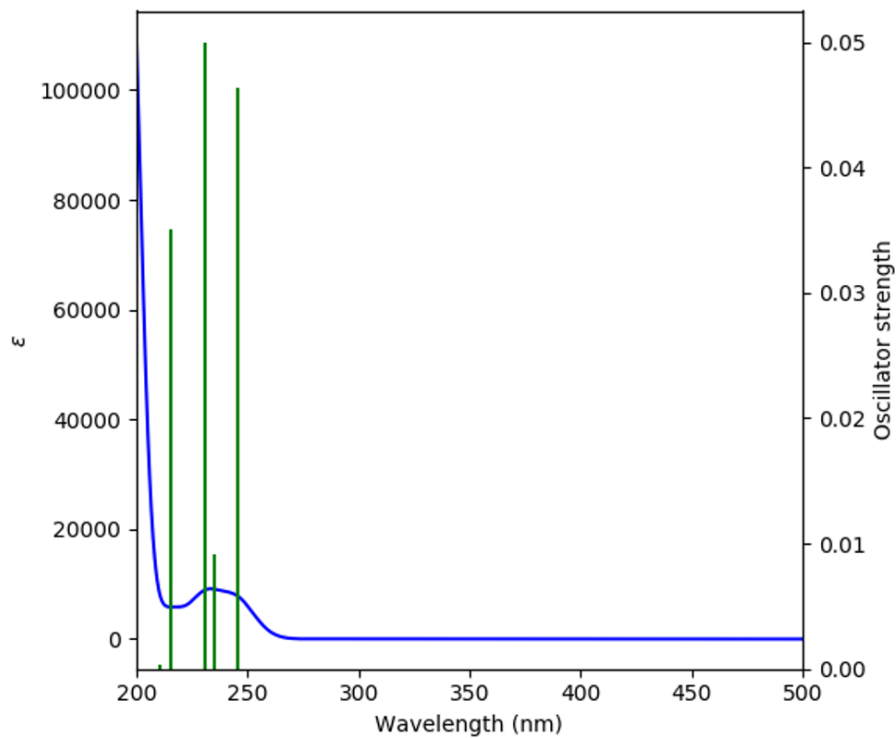
N°.	$\lambda$ (nm)	f	Major contributions (%)
1	289	0	HOMO→LUMO (97%)
2	257	0	H-3→LUMO (90%)
3	248	0	H-5→LUMO (11%), H-4→LUMO (19%), H-3→L+1 (57%)
4	248	0	H-5→LUMO (20%), H-4→LUMO (11%), H-3→L+2 (56%)
5	246	0.0464	HOMO→L+1 (87%)
6	246	0.0463	HOMO→L+2 (87%)
7	244	0	H-4→LUMO (42%), H-3→L+1 (16%)
8	244	0	H-5→LUMO (42%), H-3→L+2 (16%)
9	241	0	H-6→LUMO (70%)
10	235	0.0092	H-5→L+1 (32%), H-5→L+2 (14%), H-4→L+1 (14%), H-4→L+2 (32%)
11	234	0	H-8→LUMO (38%), H-6→L+1 (16%)
12	234	0	H-9→LUMO (38%), H-6→L+2 (15%)
13	231	0.05	H-2→L+1 (10%), H-1→LUMO (74%), H-1→L+2 (10%)
14	231	0.05	H-2→LUMO (74%), H-2→L+2 (10%), H-1→L+1 (10%)
15	229	0	H-2→L+1 (47%), H-1→L+2 (47%)
16	224	0	H-5→L+1 (24%), H-4→LUMO (14%), H-4→L+2 (24%), H-3→L+1 (10%)
17	224	0	H-5→LUMO (14%), H-5→L+2 (24%), H-4→L+1 (24%),

			H-3→L+2 (10%)
18	221	0	H-2→L+2 (45%), H-1→L+1 (44%)
19	221	0	H-6→LUMO (12%), H-5→L+1 (11%), H-5→L+2 (26%), H-4→L+1 (26%), H-4→L+2 (12%)
20	216	0.0348	H-7→L+1 (46%), H-2→L+1 (19%), H-1→L+2 (20%)
21	216	0.0351	H-7→L+2 (46%), H-2→L+2 (20%), H-1→L+1 (19%)
22	215	0	H-9→L+1 (11%), H-8→L+2 (11%), H-6→L+1 (63%)
23	215	0	H-9→L+2 (11%), H-8→L+1 (11%), H-6→L+2 (63%)
24	211	3E <sup>-4</sup>	H-9→L+1 (34%), H-9→L+2 (13%), H-8→L+1 (13%), H-8→L+2 (34%)
25	205	0	H-9→L+1 (11%), H-9→L+2 (26%), H-8→L+1 (29%), H-8→L+2 (10%), H-6→LUMO (16%)
26	205	0	H-9→L+1 (20%), H-9→L+2 (10%), H-8→LUMO (26%), H-8→L+1 (10%), H-8→L+2 (19%)
27	205	0	H-9→LUMO (25%), H-9→L+2 (21%), H-8→L+1 (18%), H-8→L+2 (10%)
28	201	0	H-7→LUMO (88%)
29	197	0.9068	H-7→L+1 (43%), H-2→L+1 (13%), H-1→LUMO (20%), H-1→L+2 (13%)
30	197	0.9064	H-7→L+2 (43%), H-2→LUMO (20%), H-2→L+2 (13%), H-1→L+1 (13%)
31	180	0	H-10→LUMO (78%)
32	180	0	H-11→LUMO (78%)
33	174	0.0033	H-12→LUMO (41%), H-11→L+1 (29%), H-10→L+2 (29%)
34	174	0	H-11→L+2 (49%), H-10→L+1 (49%)
35	170	0	H-11→LUMO (13%), H-11→L+2 (36%), H-10→L+1 (36%)
36	170	0	H-11→L+1 (36%), H-10→LUMO (13%), H-10→L+2 (36%)
37	164	3E <sup>-4</sup>	H-12→LUMO (57%), H-11→L+1 (21%), H-10→L+2 (21%)
38	163	0	H-12→L+1 (87%)
39	163	0	H-12→L+2 (87%)
40	153	8E <sup>-4</sup>	HOMO→L+3 (90%)
41	153	8E <sup>-4</sup>	HOMO→L+4 (90%)
42	152	0	H-3→L+3 (59%), H-3→L+4 (22%)
43	152	0	H-3→L+3 (22%), H-3→L+4 (59%)
44	150	0	H-14→L+1 (47%), H-13→L+2 (47%)
45	150	0.0045	H-13→LUMO (80%)
46	150	0.0045	H-14→LUMO (80%)
47	148	0	H-5→L+3 (46%), H-4→L+4 (46%)
48	146	0	H-6→L+4 (33%), H-5→L+3 (24%), H-4→L+4 (24%)
49	146	0	H-6→L+3 (33%), H-5→L+4 (24%), H-4→L+3 (24%)

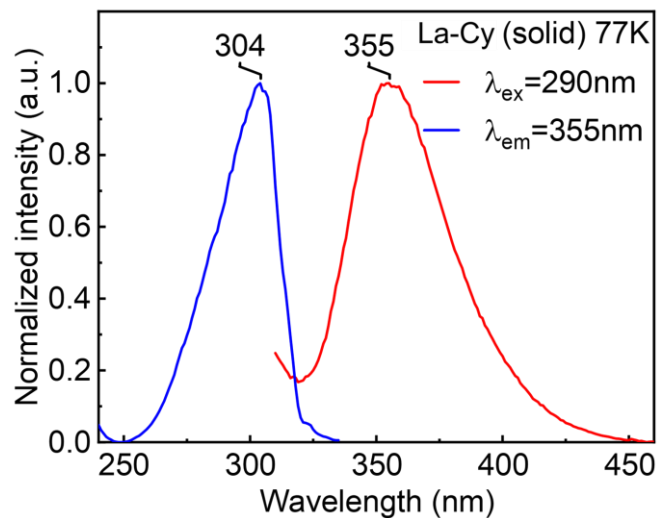


50	145	0.0163	H-14→L+1 (21%), H-13→L+2 (21%), H-2→L+4 (11%), H-1→L+3 (11%)
51	145	0.0163	H-14→L+2 (20%), H-13→L+1 (21%), H-2→L+3 (11%), H-1→L+4 (11%)
52	145	0	H-9→L+3 (44%), H-8→L+4 (44%)
53	144	0	H-14→L+2 (14%), H-13→L+1 (14%), H-2→L+3 (29%), H-1→L+4 (29%)
54	143	0	H-2→L+4 (42%), H-1→L+3 (44%)
55	143	0.0061	H-5→L+4 (46%), H-4→L+3 (47%)
56	143	2E <sup>-4</sup>	H-14→L+1 (14%), H-13→L+2 (14%), H-2→L+4 (22%), H-1→L+3 (20%)
57	143	2E <sup>-4</sup>	H-14→L+2 (14%), H-13→L+1 (14%), H-2→L+3 (21%), H-1→L+4 (21%)
58	142	0	H-6→L+3 (27%), H-5→L+4 (11%), H-4→L+3 (11%)
59	142	0	H-6→L+4 (27%), H-5→L+3 (11%), H-4→L+4 (11%)
60	140	0	H-14→L+2 (31%), H-13→L+1 (31%), H-2→L+3 (11%), H-1→L+4 (11%)
61	137	0.008	H-15→L+1 (20%), H-7→L+3 (31%), H-7→L+4 (43%)
62	137	0.008	H-15→L+2 (20%), H-7→L+3 (43%), H-7→L+4 (31%)
63	136	0	H-9→L+4 (29%), H-8→L+3 (30%), H-6→L+3 (29%)
64	136	0	H-9→L+3 (30%), H-8→L+4 (30%), H-6→L+4 (29%)
65	134	1E <sup>-4</sup>	H-9→L+4 (48%), H-8→L+3 (47%)
66	134	0	H-15→LUMO (90%)
67	133	0	HOMO→L+5 (99%)
68	132	0.0087	H-15→L+1 (65%), H-7→L+4 (12%)
69	132	0.0088	H-15→L+2 (65%), H-7→L+3 (12%)
70	131	0	H-17→LUMO (10%), H-16→LUMO (65%)
71	131	0	H-17→LUMO (65%), H-16→LUMO (10%)
72	127	0.0083	H-20→LUMO (32%), H-17→L+2 (25%), H-16→L+1 (25%)
73	126	0	H-17→L+1 (38%), H-17→L+2 (11%), H-16→L+1 (11%), H-16→L+2 (37%)
74	126	0	HOMO→L+6 (84%)
75	124	0	H-17→L+1 (33%), H-16→L+2 (34%)
76	124	0	H-17→L+2 (34%), H-16→L+1 (34%)
77	124	0	H-1→L+5 (83%)
78	124	0	H-2→L+5 (84%)
79	124	0	H-3→L+5 (89%)
80	121	0.0127	H-19→LUMO (13%), H-18→LUMO (28%), H-5→L+5 (20%), H-4→L+5 (30%)
81	121	0.0126	H-19→LUMO (28%), H-18→LUMO (14%), H-5→L+5 (30%), H-4→L+5 (20%)
82	121	0	H-3→L+6 (64%)
83	121	0.0172	H-11→L+3 (10%), H-11→L+4 (38%), H-10→L+3 (38%),

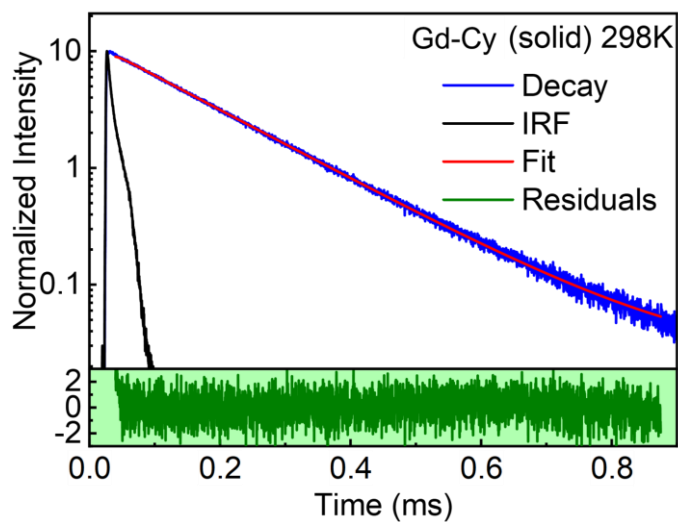
			H-10→L+4 (10%)
84	121	0.0022	H-18→LUMO (39%), H-5→L+5 (15%), H-4→L+5 (10%)
85	121	0.0023	H-19→LUMO (39%), H-5→L+5 (10%), H-4→L+5 (15%)
86	121	0	H-12→L+4 (13%), H-11→L+3 (28%), H-10→L+4 (28%)
87	121	0	H-12→L+3 (13%), H-11→L+4 (28%), H-10→L+3 (28%)
88	119	0.0089	H-19→L+1 (16%), H-19→L+2 (19%), H-18→L+1 (21%), H-18→L+2 (14%), H-5→L+5 (15%)
89	119	0.0089	H-19→L+1 (20%), H-19→L+2 (15%), H-18→L+1 (15%), H-18→L+2 (20%), H-4→L+5 (15%)
90	119	0	H-19→L+1 (15%), H-19→L+2 (22%), H-18→L+1 (20%), H-18→L+2 (16%), H-6→L+5 (12%)
91	119	0.0019	H-20→LUMO (64%), H-17→L+2 (13%), H-16→L+1 (13%)
92	118	0	H-20→L+1 (33%), H-5→L+6 (29%), H-4→L+6 (10%)
93	118	0	H-20→L+2 (32%), H-5→L+6 (10%), H-4→L+6 (29%)
94	118	0	H-19→L+1 (27%), H-19→L+2 (20%), H-18→L+1 (20%), H-18→L+2 (27%)
95	118	0	H-3→L+6 (18%), HOMO→L+7 (60%)
96	118	0.0088	H-1→L+6 (88%)
97	118	0.0088	H-2→L+6 (88%)
98	118	0	H-20→L+1 (56%), H-5→L+6 (20%)
99	118	0	H-20→L+2 (57%), H-4→L+6 (20%)
100	117	0.0039	H-7→L+5 (97%)



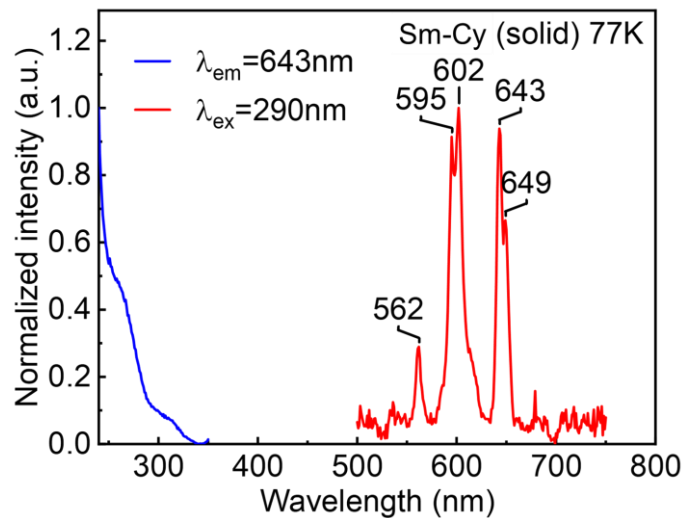
**Figure S24.** Simulated absorption spectrum for  $\text{Cy}^{3-}$  in the gas phase by TDDFT computations. Bar graph reporting the calculated oscillator strength and the calculated position of the 100th electronic transitions calculated by TDDFT for  $\text{Cy}^{3-}$  in the gas phase (bar graph;  $f$  = computed oscillator strength).



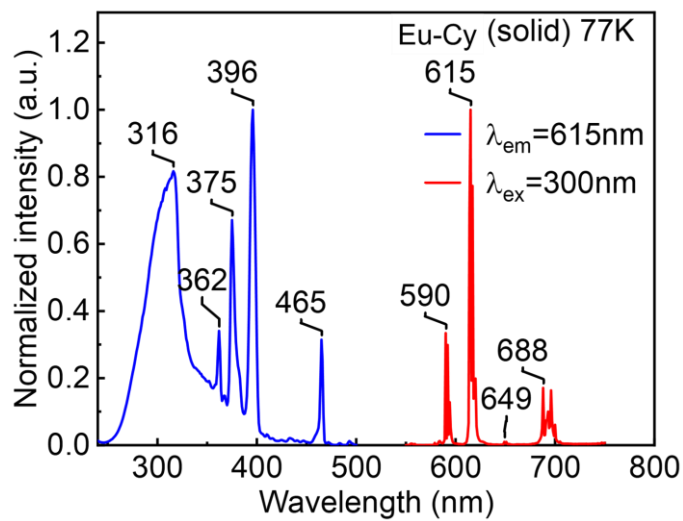
**Figure S25.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for La-Cy at 298 K ( $\lambda_{\text{ex}} = 270$  nm,  $\lambda_{\text{em}} = 335$  nm) and 77K ( $\lambda_{\text{ex}} = 270$  nm,  $\lambda_{\text{em}} = 355$  nm).



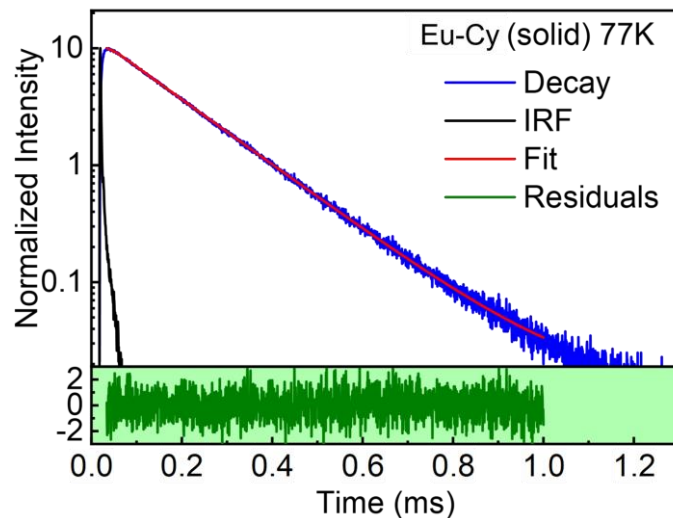
**Figure S26.** Decay of emission intensity, fit, IRF and residual of Gd-Cy at 298 K.  $\lambda = 339$  nm ( $\lambda_{\text{ex}} = 277$  nm),  $\tau_e \{f\% \} = 15 \mu\text{s} \{100\}$ ,  $\chi^2 = 1.070$ .



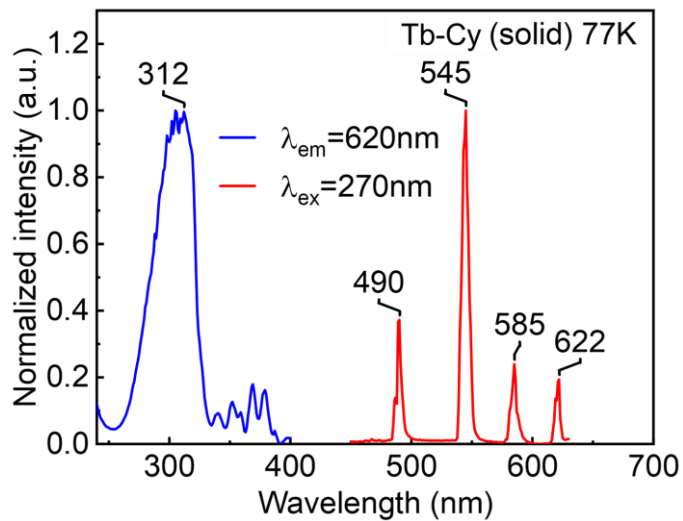
**Figure S27.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for Sm-Cy at 77K ( $\lambda_{ex} = 290$  nm,  $\lambda_{em} = 643$  nm).



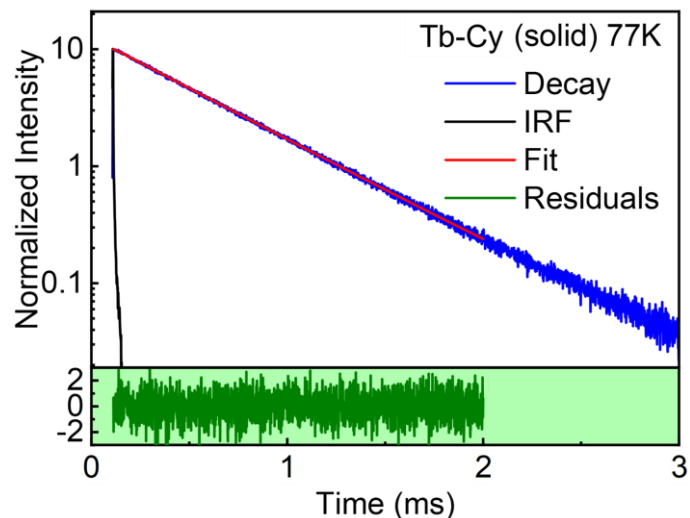
**Figure S28.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for Eu-Cy at 77K ( $\lambda_{ex} = 300$  nm,  $\lambda_{em} = 615$  nm).



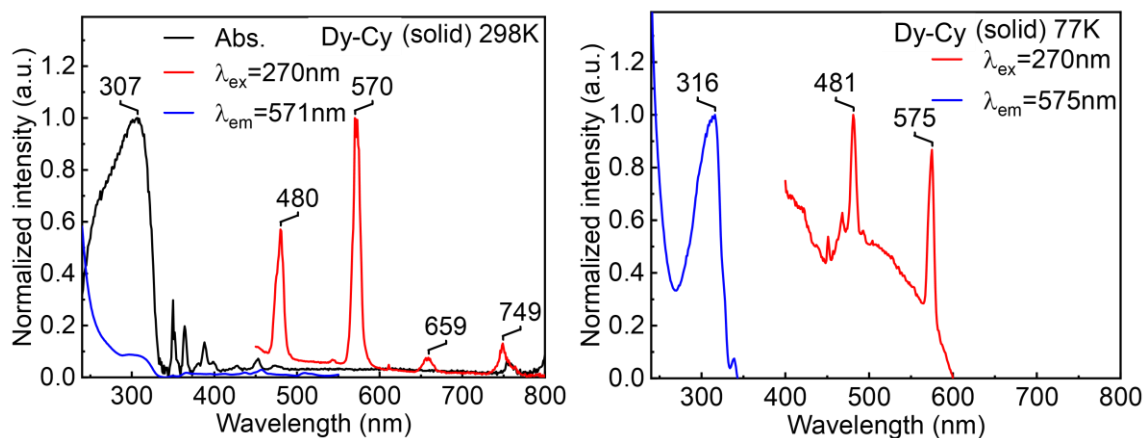
**Figure S29.** Decay of emission intensity, fit, IRF and residual of Eu-Cy. Left at 77 K  $\lambda = 615$  nm ( $\lambda_{\text{ex}} = 300$  nm),  $\tau_e$  {f%} = 16  $\mu\text{s}$  {100},  $\chi^2 = 1.001$ .



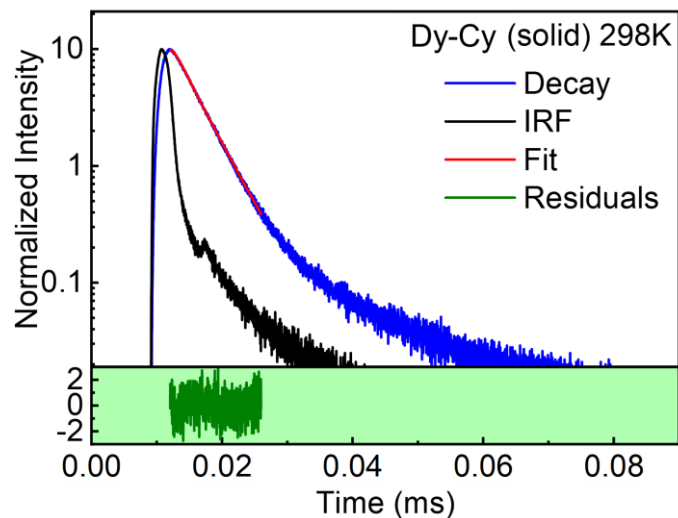
**Figure S30.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for Tb-Cy at 77K ( $\lambda_{\text{ex}} = 270$  nm,  $\lambda_{\text{em}} = 620$  nm).



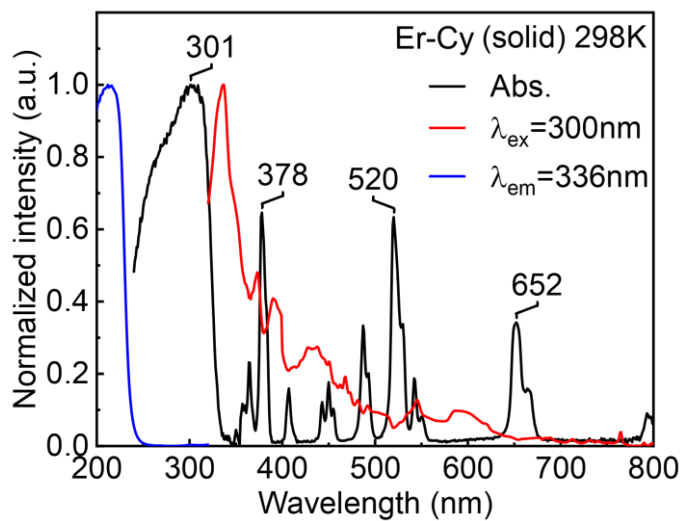
**Figure S31.** Decay of emission intensity, fit, IRF and residual of Tb-Cy. Left, at 77 K  $\lambda = 620$  nm ( $\lambda_{\text{ex}} = 270$  nm),  $\tau_e$  {f%} = 50  $\mu\text{s}$  {100},  $\chi^2 = 1.031$ .



**Figure S32.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for Dy-Cy at 298 K ( $\lambda_{\text{ex}} = 270$  nm,  $\lambda_{\text{em}} = 571$  nm) and 77K ( $\lambda_{\text{ex}} = 270$  nm,  $\lambda_{\text{em}} = 575$  nm).

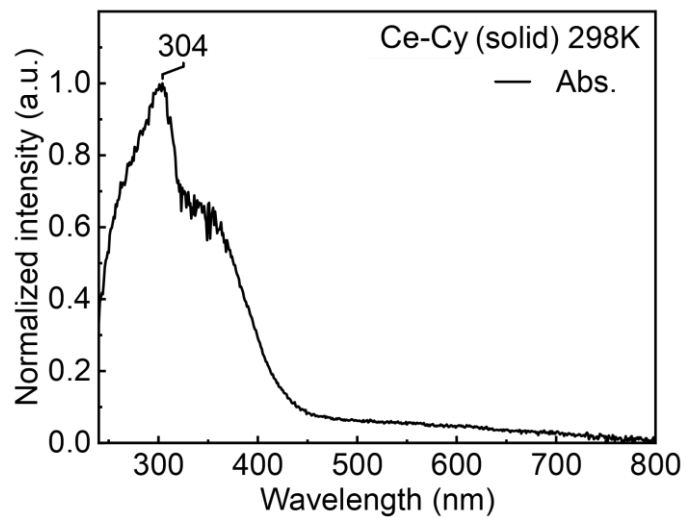


**Figure S33.** Decay of emission intensity, fit, IRF and residual of Dy-Cy at 298 K.  $\lambda = 570$  nm ( $\lambda_{\text{ex}} = 270$  nm),  $\tau_e$  {f%} = 3.48  $\mu\text{s}$  {100},  $\chi^2 = 1.034$ .

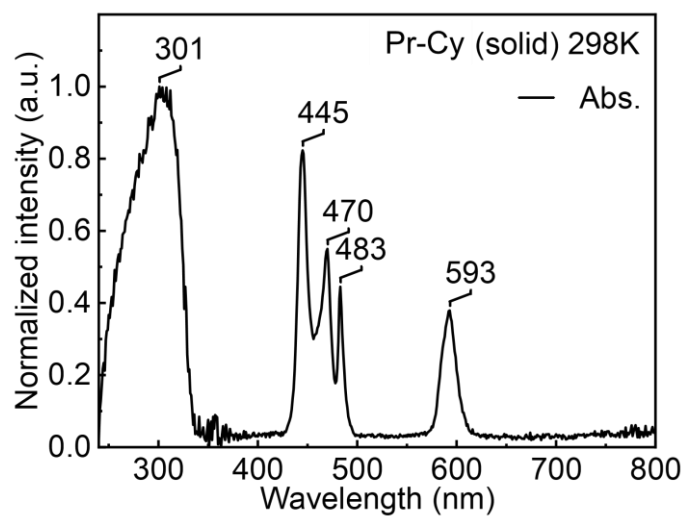


**Figure S34.** Solid-state absorption (black), emission (red) and excitation (blue) spectra for Er-Cy at 298 K ( $\lambda_{\text{ex}} = 300$  nm,  $\lambda_{\text{em}} = 336$  nm).

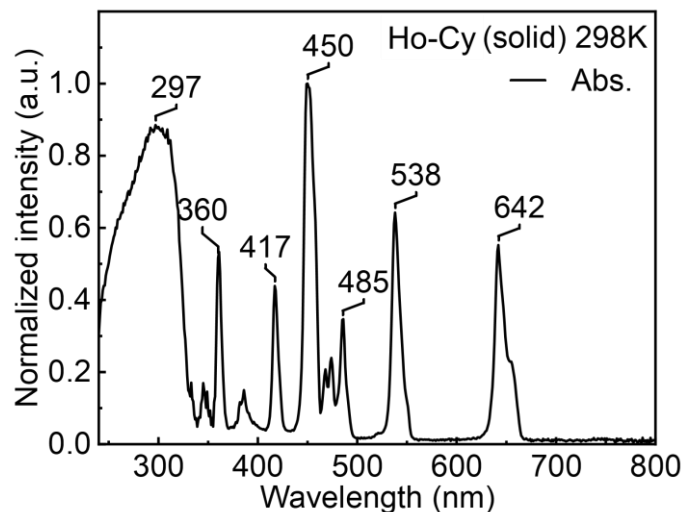




**Figure S35.** Solid-state absorption (black) spectra for Ce-Cy at 298 K.



**Figure S36.** Solid-state absorption (black) spectra for Pr-Cy- at 298 K.



**Figure S37.** Solid-state absorption (black) for Ho-Cy at 298 K.

**Table S8.** Photophysical properties of all emissive Ln-Cy.

Photophysical series		T(K)	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	Corresponding transitions	$\tau_e$ {f%}	$\chi^2$
(A) only the ligand is emissive in the visible region	La-Cy	298	270	360	$\pi \rightarrow \pi^*$	3.3 $\mu$ s {67.80}, 76.2 $\mu$ s {32.20}	1.044
	Gd-Cy	298	277	339		15 $\mu$ s {100}	1.070
	Tm-Cy	298	270	620		----	----
(B) both ligand and lanthanide metal are emissive in the visible region	Yb-Cy	298	270	328	$\pi \rightarrow \pi^*$ ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$	----	----
(C) only the lanthanide metal is emissive in the visible region	Sm-Cy	298	310	641	${}^4G_{5/2} \rightarrow {}^6H_{9/2}$	44.9 $\mu$ s {6.4}, 270 $\mu$ s {8.5}, 1.1 ms {16.3}, 4.0 ms {68.9}	1.072
	Eu-Cy	298	300	615	${}^5D_0 \rightarrow {}^4F_2$	6.7 $\mu$ s {2.37}, 150 $\mu$ s {89.5}, 53 $\mu$ s {8.1}	1.004
	Tb-Cy	298	270	545	${}^5D_4 \rightarrow {}^4F_5$	49 $\mu$ s {100}	1.021
	Dy-Cy	298	270	570	${}^4F_{9/2} \rightarrow {}^6H_{13/2}$	3.48 $\mu$ s {100}	1.034
	Er-Cy	298	300	336	${}^4S_{3/2} \rightarrow {}^4I_{15/2}$	----	----