SUPPORTING INFORMATION

Wide Range UV–to–Visible Excitation of Near-Infrared Emission and Slow Magnetic Relaxation in Ln^{III}(4,4'-Azopyridine-1,1'-Dioxide)[Co^{III}(CN)₆]^{3–} Layered Frameworks

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Figure S1. Infrared absorption spectra of **1–6** shown in the broad wavenumber measurement range of 4000–900 cm⁻¹ (*a*), and the limited range of 2200–2060 cm⁻¹ indicating the absorption bands related to the stretching vibrations of cyanide ligands (*b*).



Figure S2. Thermogravimetric curves of 1–6 collected in the temperature range of 20–375 °C. Two main steps related to the expected loss of crystallization and coordination water molecules were depicted. The experiments were performed under an air atmosphere with the heating rate of 1 °C per minute.

Comment to Figure S2

The powder samples of 1-6 exhibit the stable composition on heating from temperature to ca. 50–60 °C. The thermal stability increases on going from light to heavy lanthanides. The lowest thermal stability is assigned to 1 (NdCo) and 2 (TbCo) exhibiting the first step in the TGA curve above 45-50 °C, while the highest thermal stability is characteristic of 5 (TmCo) and 6 (YbCo) revealing the stable composition up to 60 $^{\circ}$ C. The first step in the TGA curve is positioned within the 50-60 °C range, and the related weight loss is ca. 7-8 %, depending on the lanthanide. Such decrease is slightly higher than the 5.1–5.3 % range, expected for the loss of two weakly bonded crystallization water molecules. It indicates that this first step in the TGA curves of 1-6 can be assigned mainly to the removal of crystallization water molecules, and presumably one of four coordinated water molecules per {LnCo} unit. This first weight loss is followed by a narrow thermal stability of the compounds composition to ca. 100 °C. Further heating leads to the continuous decrease of the mass in the very broad 100–190 °C region. In most of the compounds, the related weight loss on heating is rather featureless, and the visible multiple steps could be only detected for 1. At 190 °C, the detected total weight loss is 14–15.4 °C which corresponds well to the mass loss of 15.2–16 °C expected for the removal of all water molecules. It indicates that above 190 °C, 1–6 undergo the phase transition to the fully dehydrated form, {[Ln^{III}(apdo)][Co^{III}(CN)₆]}. The resulting dehydrated phases are stable upon further heating in the broad temperature range up to 280 °C. At higher temperatures, the abrupt large decrease of the mass is observed, and it can be explained by the removal of terminal cyanides, and the gradual decomposition of apdo ligands.



Figure S3. Comparison of the asymmetric units of 1(a), 2(b), 3(c), 4(d), 5(e), and 6(f) presented with the atoms labelling schemes. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms were shown as fixed-size spheres of 0.15 Å radius. The related bond lengths and angles are gathered in Table S1.



Figure S4. The supramolecular arrangement of the coordination layers and crystallization water molecules of 1 presented along the crystallographic a axis (a), b axis (b), and c axis (c).



Figure S5. The hydrogen bonding network of 1 with the labelling of the atoms directly involved in the hydrogen bonds. The representative views within the bc (*a*) and (101) (*b*) crystallographic planes are presented. The analogous hydrogen bonding networks are detected in 2–6 compounds. The interatomic distances related to the presented hydrogen bonds are gathered for 1–6 in Table S3.

Details of $[Ln^{III}(\mu-apdo)_2(H_2O)_4(\mu-NC)_2]^+$ complexes						
Parameter	1 (Ln = Nd)	2 (Ln = Tb)	3 (Ln = Dy)	4 (Ln = Er)	5 (Ln = Tm)	6 (Ln = Yb)
Ln1–N1	2.538(4) Å	2.451(4) Å	2.433(2) Å	2.402(2) Å	2.390(3) Å	2.382(2) Å
Ln1–N6	2.558(3) Å	2.473(4) Å	2.462(2) Å	2.435(2) Å	2.424(3) Å	2.416(2) Å
Ln1–O1	2.511(3) Å	2.429(3) Å	2.414(2) Å	2.388(2) Å	2.373(2) Å	2.363(2) Å
Ln1–O2	2.453(3) Å	2.380(3) Å	2.367(2) Å	2.342(2) Å	2.331(2) Å	2.323(2) Å
Ln1–O3	2.607(4) Å	2.568(4) Å	2.561(2) Å	2.552(2) Å	2.554(3) Å	2.552(3) Å
Ln1–O4	2.396(3) Å	2.323(3) Å	2.313(2) Å	2.292(2) Å	2.282(2) Å	2.265(2) Å
Ln1–O5	2.361(3) Å	2.310(3) Å	2.300(2) Å	2.283(2) Å	2.277(2) Å	2.268(2) Å
Ln1–O6	2.370(3) Å	2.309(3) Å	2.298(2) Å	2.279(2) Å	2.270(2) Å	2.260(2) Å
Ln1–N1–C1	161.8(4)°	164.1(4)°	164.7(2)°	166.0(2)°	166.0(3)°	166.3(2)°
Ln1–N6–C6	172.2(3)°	173.0(3)°	173.26(18)°	173.3(2)°	173.4(2)°	174.0(2)°
Ln1-O5-N7	151.1(3)°	149.1(3)°	149.01(14)°	148.62(15)°	148.49(18)°	148.13(17)°
Ln1-O6-N9	127.6(2)°	127.4(2)°	127.54(13)°	127.47(14)°	127.31(17)°	126.90(16)°
N1-Ln1-N6	77.15(13)°	77.55(13)°	77.88(7)°	78.28(8)°	78.48(9)°	78.65(9)°
O5-Ln1-O6	76.75(11)°	79.46(11)°	79.78(6)°	80.31(7)°	80.46(8)°	80.86(8)°
Ln1–Ln1'	14.91 Å	14.80 Å	14.77 Å	14.73 Å	14.71 Å	14.68 Å
(through apdo)	15.97 Å	15.85 Å	15.82 Å	15.78 Å	15.76 Å	15.74 Å
other ^a	7.31 Å	7.41 Å	7.42 Å	7.46 Å	7.47 Å	7.48 Å
Lni–Lni	8.33 A	8.21 A	8.19 A	8.15 A	8.12 A	8.10 A
		Details o	$f \left[Co^{III}(CN)_6 \right]^{3-} co$	omplexes		
Parameter	1	2	3	4	5	6
Co1–C1	1.877(4) Å	1.886(5) Å	1.883(2) Å	1.883(2) Å	1.888(3) Å	1.885(3)
Co1–C2	1.886(5) Å	1.890(5) Å	1.891(2) Å	1.893(3) Å	1.893(3) Å	1.895(3)
Co1–C3	1.896(4) Å	1.890(5) Å	1.899(2) Å	1.901(3) Å	1.901(3) Å	1.902(3)
Co1–C4	1.891(4) Å	1.895(5) Å	1.892(2) Å	1.895(2) Å	1.896(3) Å	1.895(3)
Co1–C5	1.886(4) Å	1.888(5) Å	1.890(2) Å	1.888(3) Å	1.895(3) Å	1.892(3)
Co1–C6	1.892(4) Å	1.897(5) Å	1.895(2) Å	1.896(2) Å	1.902(3) Å	1.900(3)
C–N	1.139(6)– 1.150(6) Å	1.143(6)– 1.151(5) Å	1.139(3)– 1.151(3) Å	1.137(3)– 1.151(3) Å	1.135(4)– 1.146(4) Å	1.137(4)– 1.145(4) Å
Co1C1N1	177.5(4)°	177.0(4)°	176.8(2)°	176.6(2)°	176.4(3)°	176.9(3)°
Co1-C2-N2	176.5(4)°	176.4(5)°	176.3(3)°	176.4(3)°	176.6(3)°	176.6(3)°
Co1-C3-N3	179.0(4)°	178.3(4)°	178.3(2)°	178.4(2)°	177.9(3)°	177.6(3)°
Co1-C4-N4	176.2(4)°	175.2(4)°	175.8(2)°	175.9(2)°	175.3(3)°	175.9(3)°
Co1-C5-N5	178.8(4)°	178.7(5)°	178.9(2)°	179.2(3)°	179.4(3)°	179.3(3)°
Co1-C6-N6	178.2(4)°	178.6(4)°	178.5(2)°	178.7(2)°	178.7(3)°	174.0(2)°
Co1–Ln1 distances	5.496 Å 5.580 Å	5.425 Å 5.508 Å	5.413 Å 5.495 Å	5.390 Å 5.471 Å	5.379 Å 5.460 Å	5.368 Å 5.448 Å

 Table S1. Detailed structure parameters of 1–6.

^a Other Ln1–Ln1' distances include those within the cyanido-bridged $\{Ln_2Co_2\}$ squares, and between these squares within the same coordination layer.

Table S2. Results of Continuous Shape Measure Analysis for $[Ln^{III}(\mu-apdo)_2(H_2O)_4(\mu-NC)_2]^+$ complexes in the crystal structures of **1–6**.

Compound		Coordina		
	BTP-8	SAPR-8	DD-8	Geometry
1	2.006	2.066	0.518	DD-8
2	1.889	1.668	0.642	DD-8
3	1.905	1.667	0.668	DD-8
4	1.893	1.601	0.707	DD-8
5	1.893	1.556	0.740	DD-8
6	1.921	1.559	0.773	DD-8

* CSM parameters:

CSM BTP-8 = the parameter related to the bicapped trigonal prism geometry (C_{2v} symmetry)

CSM SAPR-8 = the parameter related to the square antiprism (D_{4d} symmetry)

CSM DD-8 = the parameter related to the dodecahedron (D_{2d} symmetry)

CSM = 0 for the ideal geometry and the increase of CSM parameter corresponds to the increasing distortion from the ideal polyhedron.

References: (*a*) Llunell, M.; Casanova, D.; Cirera, J.; Bofill, J.; Alemany, P.; Alvarez, S.; Pinsky, M.; Avnir, D. *SHAPE v. 2.1. Program for the Calculation of Continuous Shape Measures of Polygonal and Polyhedral Molecular Fragments*, University of Barcelona: Barcelona, Spain, 2013; (*b*) Casanova, D.; Cirera, J.; Llunell, M.; Alemany, P.; Avnir, D.; Alvarez, S. Minimal Distortion Pathways in Polyhedral Rearrangements. *J. Am. Chem. Soc.* **2004**, *126*, 1755–1763.

Parameter	1 (Ln = Nd)	2 (Ln = Tb)	3 (Ln = Dy)	4 (Ln = Er)	5 (Ln = Tm)	6 (Ln = Yb)
O1–(H1A)–N5	2.90 Å	2.86 Å	2.85 Å	2.84 Å	2.84 Å	2.83 Å
O1–(H1B)–N2	3.05 Å	3.08 Å	3.09 Å	3.11 Å	3.12 Å	3.12 Å
O2–(H2A)–O8	2.77 Å	2.76 Å				
O2-(H2B)-N3	2.83 Å	2.84 Å				
O3–(H3A)–O3	3.00 Å	2.99 Å	3.02 Å	3.01 Å	3.01 Å	3.01 Å
O3–(H3B)–N1	3.63 Å	3.74 Å	3.76 Å	3.80 Å	3.82 Å	3.84 Å
O4-(H4A)-N4	2.77 Å	2.77 Å	2.77 Å	2.78 Å	2.78 Å	2.78 Å
O4–(H4B)–O7	2.60 Å	2.61 Å	2.61 Å	2.61 Å	2.61 Å	2.62 Å
O7-(H7A)-N3	3.12 Å	3.12 Å	3.11 Å	3.12 Å	3.12 Å	3.12 Å
O7-(H7B)-N8	3.64 Å	3.76 Å	3.79 Å	3.86 Å	3.87 Å	3.90 Å
O8–(H8A)–N2	2.84 Å	2.82 Å	2.82 Å	2.81 Å	2.81 Å	2.81 Å
O8–(H8B)–N5	2.90 Å	2.90 Å	2.90 Å	2.91 Å	2.92 Å	2.91 Å

Table S3. Detailed interatomic distances of hydrogen bonding network of 1–6. The related hydrogen bonds arevisualized in Figure S5.



Figure S6. Experimental (exp) powder X-ray diffraction (PXRD) patterns of the polycrystalline samples of **1–6** confronted with the respective PXRD patterns calculated (calcd) on the basis of the structural models obtained from single-crystal X-ray structural analyses.



Figure S7. Full magnetic-field-variable alternate-current (*ac*) magnetic susceptibility characteristics of **1** at T = 1.8 K, under $H_{ac} = 1$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} " (*b*) at various indicated *dc* external magnetic fields, together with the related Argand plots (*c*), and the field dependence of the relaxation time, τ (*d*). Both field, and relaxation time were presented in (*d*) in the logarithmic scale. The relaxation times in (*d*) were shown for both the faster field-independent relaxation (blue points), and the slower field-dependent relaxation process (black points). Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for two relaxation processes. The solid red line in (*d*) shows the best fit taking into account quantum tunneling of magnetization, and direct process for the range of 800–8000 Oe.



Figure S8. Full temperature-variable alternate-current (*ac*) magnetic susceptibility characteristics of **1** under $H_{ac} = 1$ Oe, $H_{dc} = 4500$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} '' (*b*) at various indicated temperatures, together with the related Argand plots (*c*), and the temperature dependence of the relaxation time, τ (*d*). The relaxation times in (*d*) were shown for both the faster temperature-independent relaxation (blue points), and the slower temperature-dependent relaxation process (black points). Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for two relaxation processes. The solid blue line in (*d*) represents the linear fitting for the limited range of 3.0–3.5 K, following the Arrhenius law, when the red line shows the best fit taking into account the Orbach and Raman relaxation processes, quantum tunneling of magnetization, and direct process for the broader range of 1.8–3.5 K.



Figure S9. Full magnetic-field-variable alternate-current (*ac*) magnetic susceptibility characteristics of **3** at T = 1.8 K, under $H_{ac} = 1$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} " (*b*) at various indicated *dc* external magnetic fields, together with the related Argand plots (*c*), and the field dependence of the relaxation time, τ (*d*). Both field, and relaxation time were presented in (*d*) in the logarithmic scale. The relaxation times in (*d*) were shown for both the faster field-independent relaxation (blue points), and the slower field-dependent relaxation process (black points). Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for two relaxation processes. The solid red line in (*d*) shows the best fit taking into account quantum tunneling of magnetization, and direct process for the range of 400–5000 Oe.



Figure S10. Full temperature-variable alternate-current (*ac*) magnetic susceptibility characteristics of **3** under $H_{ac} = 1$ Oe, $H_{dc} = 1500$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} '' (*b*) at various indicated temperatures, together with the related Argand plots (*c*), and the temperature dependence of the relaxation time, τ (*d*). The relaxation times in (*d*) were shown for both the slower temperature-independent relaxation (blue points), and the faster temperature-dependent relaxation process (black points). Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for two relaxation processes. The solid blue line in (*d*) represents the linear fitting for the limited range of 4.0–4.6 K, following the Arrhenius law, when the red line shows the best fit taking into account the Orbach and Raman relaxation processes, quantum tunneling of magnetization, and direct process for the broader range of 1.8–4.6 K.



Figure S11. Full magnetic-field-variable alternate-current (*ac*) magnetic susceptibility characteristics of **6** at T = 1.9 K, under $H_{ac} = 3$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} '' (*b*) at various indicated *dc* external magnetic fields, together with the related Argand plots (*c*), and the field dependence of the relaxation time, τ (*d*). Both field, and relaxation time were presented in (*d*) in the logarithmic scale. The relaxation times were only shown for the faster relaxation process related to the frequency range of 100–1500 Hz. Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for a single relaxation (100–800 Oe), or two relaxation processes (1000–3000 Oe). The solid red line in (*d*) shows the best fit taking into account quantum tunneling of magnetization, and direct process for the range of 100–3000 Oe.



Figure S12. Full temperature-variable alternate-current (*ac*) magnetic susceptibility characteristics of **6** under $H_{ac} = 3$ Oe, $H_{dc} = 700$ Oe, and their analysis: frequency dependences of the in-phase susceptibility, χ_{M} ' (*a*), and the out-of-phase susceptibility, χ_{M} '' (*b*) at various indicated temperatures, together with the related Argand plots (*c*), and the temperature dependence of the relaxation time, τ (*d*). Colored solid curves in (*a*), (*b*), and (*c*) represent the best fits using the generalized Debye model for a single relaxation. The solid blue line in (*d*) represents the linear fitting for the limited range of 4.0–4.6 K, following the Arrhenius law, when the red line shows the best fit taking into account the Orbach and Raman relaxation processes, quantum tunneling of magnetization, and direct process for the broader range of 1.85–4.6 K.

Comment to Figures S5–S10. Equations used for fitting the *ac* magnetic susceptibility plots.

The following equations related to the generalized Debye model for two relaxation processes were applied for compounds 1 and 3 (Figures S5–S8):

$$\chi'(\omega) = \chi_{s,total} + \Delta \chi_1 \frac{1 + (\omega\tau_1)^{1-\alpha_1} \sin(\frac{\pi\alpha_1}{2})}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\frac{\pi\alpha_1}{2}) + (\omega\tau_1)^{2(1-\alpha_1)}} + \Delta \chi_2 \frac{1 + (\omega\tau_2)^{1-\alpha_2} \sin(\frac{\pi\alpha_2}{2})}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\frac{\pi\alpha_2}{2}) + (\omega\tau_2)^{2(1-\alpha_2)}}$$
$$\chi''(\omega) = \Delta \chi_1 \frac{(\omega\tau_1)^{1-\alpha_1} \cos(\frac{\pi\alpha_1}{2})}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\frac{\pi\alpha_1}{2}) + (\omega\tau_1)^{2(1-\alpha_1)}} + \Delta \chi_2 \frac{(\omega\tau_2)^{1-\alpha_2} \cos(\frac{\pi\alpha_2}{2})}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\frac{\pi\alpha_2}{2}) + (\omega\tau_2)^{2(1-\alpha_2)}}$$

where

 $\chi_{S,total}$ is the sum of the adiabatic susceptibility of two relaxation processes ($\chi_{S,1} + \chi_{S,2}$),

 $\Delta \chi_1$ is the difference between the adiabatic susceptibility ($\chi_{S,1}$) and the isothermal susceptibility ($\chi_{T,1}$) of the first relaxation process,

 $\Delta \chi_2$ is the difference between the adiabatic susceptibility ($\chi_{S,2}$) and the isothermal susceptibility ($\chi_{T,2}$) of the second relaxation process,

 τ_1 and τ_2 are the relaxation times of the first and the second relaxation processes, respectively,

 α_1 and α_2 are the distribution (Cole-Cole) parameters of the first and the second relaxation processes, respectively, and ω is an angular frequency, that is $\omega = 2\pi v$, with v stands for the linear frequency in the [Hz] units.

In the case of compound 6 (Figures S9–S10), the following equations of the generalized Debye model for single relaxation process were used:

$$\chi'(\omega) = \chi_{S} + (\chi_{T} - \chi_{S}) \frac{1 + (\omega\tau)^{1-\alpha} \sin(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\pi\alpha/2) + (\omega\tau)^{2(1-\alpha)}}$$
$$\chi''(\omega) = (\chi_{T} - \chi_{S}) \frac{(\omega\tau)^{1-\alpha} \cos(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\pi\alpha/2) + (\omega\tau)^{2(1-\alpha)}}$$

where

 $\chi_{\rm S}$ is the adiabatic susceptibility (at infinitely high frequency of *ac* field),

 $\chi_{\rm T}$ is the isothermal susceptibility (at infinitely low frequency of *ac* field),

 τ is the relaxation time,

 α is the distribution (Cole-Cole) parameter,

and ω is an angular frequency, that is $\omega = 2\pi v$, with v stands for the linear frequency in the [Hz] units

References: (*a*) Guo, Y.-N.; Xu, G.-F.; Guo, Y.; Tang, J. Relaxation dynamics of dysprosium(III) single molecule magnets. *Dalton Trans.* **2011**, *40*, 9953–9963; (*b*) Ramos Silva, M.; Martin-Ramos, P.; Coutinho, J. T.; Pereira, L. C. J.; Martin-Gil, J. Effect of the capping ligand on luminescent erbium(III) β-diketonate single-ion magnets. *Dalton Trans.* **2014**, *43*, 6752–6761.



Figure S13. Alternate-current (*ac*) magnetic data for 2 – frequency dependences of the out-of-phase susceptibility, $\chi_{\rm M}$ ", at various indicated external *dc* magnetic fields at T = 1.8 K (*a*), and at various indicated temperatures at $H_{\rm dc} = 1500$ Oe (*b*). For all measurements, $H_{\rm ac} = 1$ Oe. The solid lines are only to guide the eye.



Figure S14. Alternate-current (*ac*) magnetic data for **4** – frequency dependences of the out-of-phase susceptibility, $\chi_{\rm M}$ ", at various indicated external *dc* magnetic fields at T = 1.8 K (*a*), and at various indicated temperatures under $H_{\rm dc} = 800$ Oe (*b*), and $H_{\rm dc} = 2000$ Oe (*c*). For all measurements, $H_{\rm ac} = 3$ Oe. The solid lines are only to guide the eye.



Figure S15. Alternate-current (*ac*) magnetic data for **5** – frequency dependences of the out-of-phase susceptibility, χ_M ", at various indicated external *dc* magnetic fields at T = 1.9 K (*a*), and at various indicated temperatures at $H_{dc} = 4000$ Oe (*b*). For all measurements, $H_{ac} = 3$ Oe. The solid lines are only to guide the eye.



Figure S16. UV-Vis-NIR absorption spectra of **1–6** compared with the respective spectra of apdo ligand and $K_3[Co(CN)_6]$: (*a*) the full set of all the spectra, and (*b*) the separated spectra of the indicated compounds.



Figure S17. Comparison of the UV–Vis–NIR absorption spectra of **1–6** (*a*) and the apdo ligand (*b*) with the position of the expected (not detected) emission signals form Tb(III), Dy(III), and Tm(III) in the visible range with the underlined emissive states (*c*), and the observed emission from Nd(III) and Yb(III) in the NIR range, along with the expected emission of Er(III) (*d*). Reference: Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048–1077.