

Supporting Information

Structural, thermal and functional properties of a hybrid dicyanamide-perovskite solid solution.

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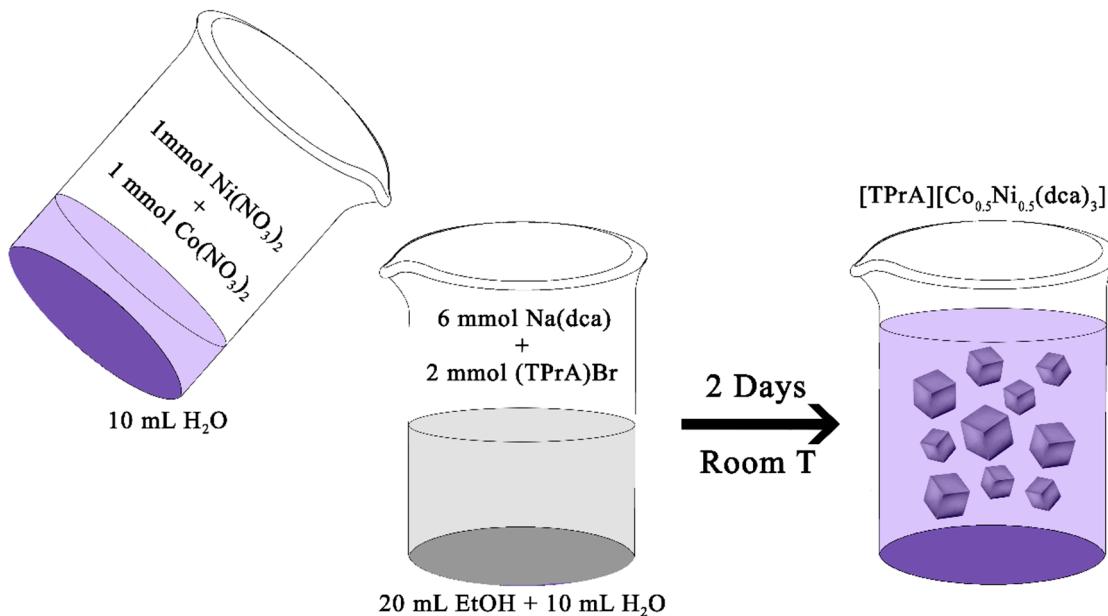
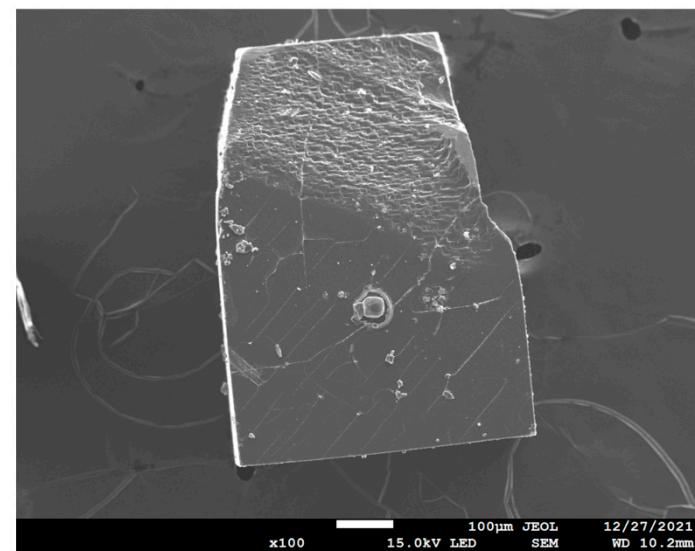
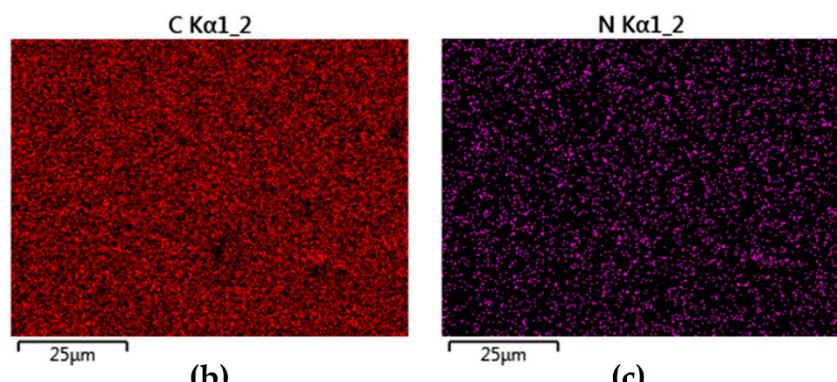


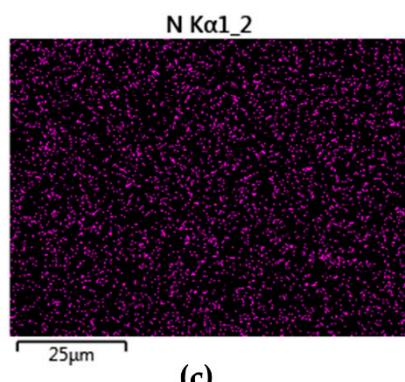
Figure S1. Synthesis scheme of $[TPrA][Co_{0.5}Ni_{0.5}(dca)_3]$ by slow evaporation.



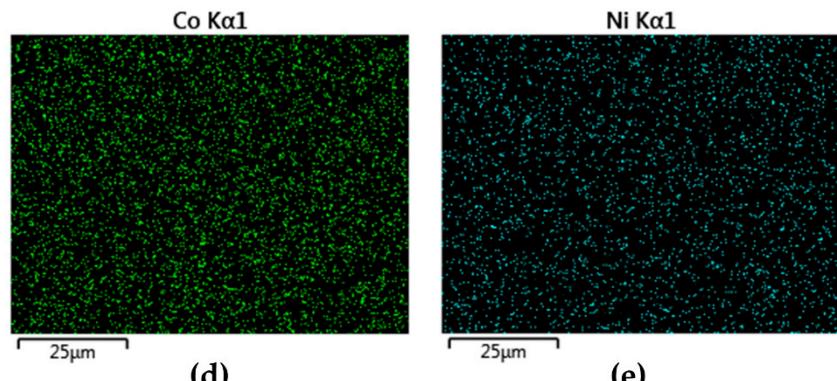
(a)



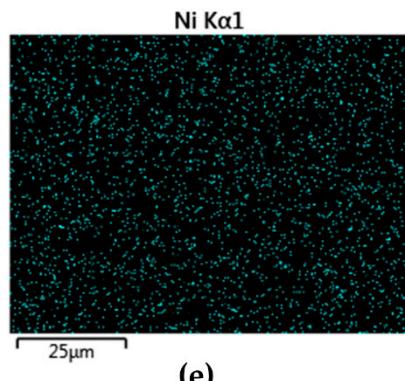
(b)



(c)



(d)



(e)

Figure S2. (a) Scanning Electron Microscopy image of the [TPrA][Co_{0.5}Ni_{0.5}(dca)₃], X-ray map of (b) carbon, (c) nitrogen, (d) cobalt and (e) nickel.

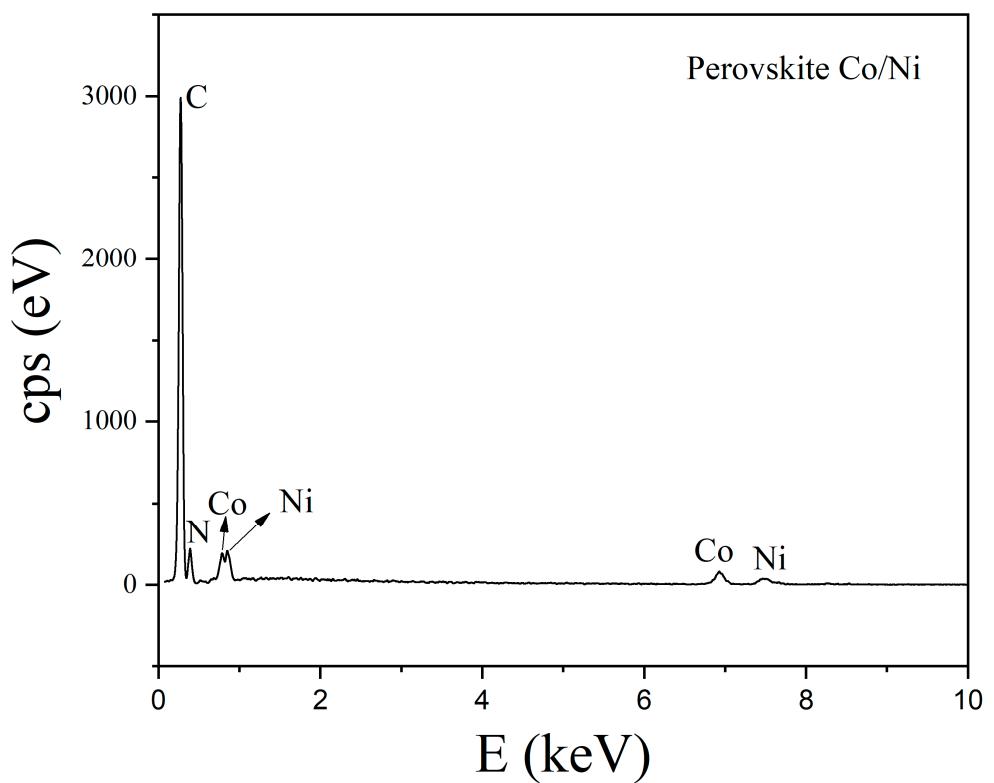


Figure S3. EDS spectrum of the [TPrA][Co_{0.5}Ni_{0.5}(dca)₃].

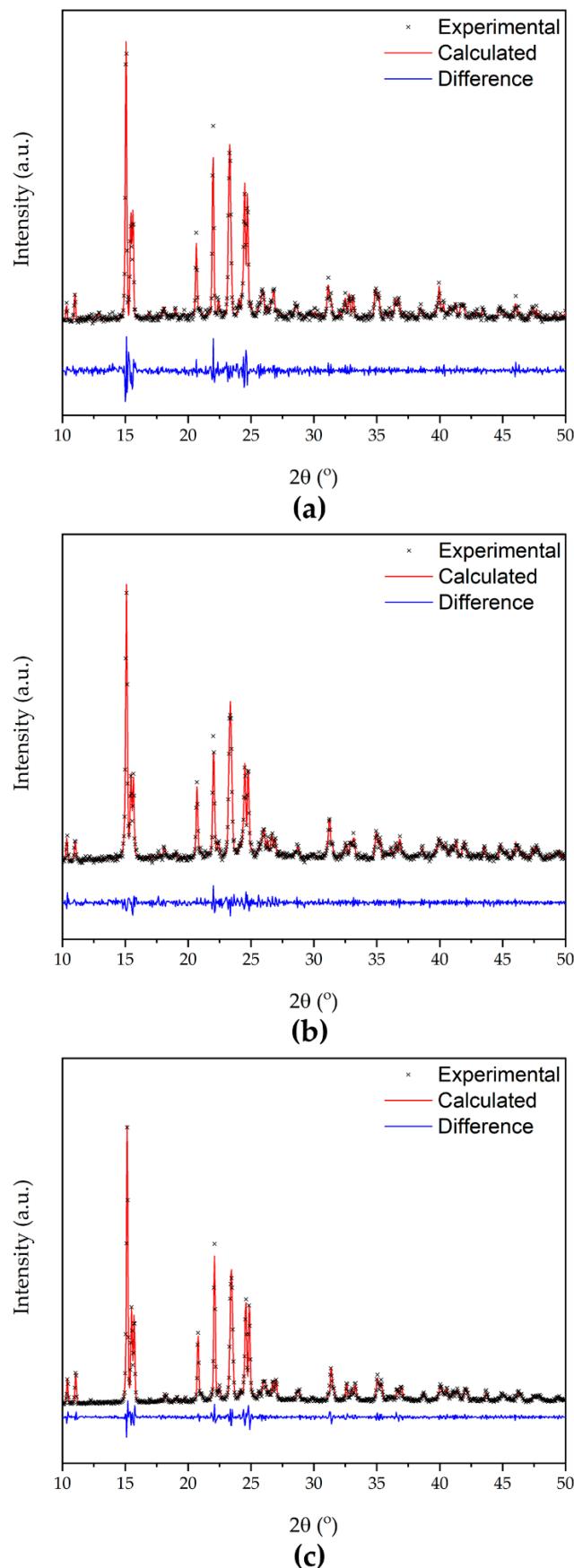


Figure S4. Le Bail refinements of the (a) [TPrA][Co(dca)₃], (b) [TPrA][Co_{0.5}Ni_{0.5}(dca)₃] and (c) [TPrA][Ni(dca)₃].

Table S1. Crystal data and structure refinement for [TPrA][Co_{0.5}Ni_{0.5}(dca)₃].

| | |
|---|--|
| Empirical formula | C ₃₆ H ₂₈ CoN ₂₀ Ni |
| Formula weight | 73.06 |
| Temperature/K | 100 |
| Crystal system | tetragonal |
| Space group | P-42 ₁ C |
| a/Å | 16.0652(12) |
| b/Å | 16.0652(12) |
| c/Å | 17.0550(12) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å ³ | 4401.7(7) |
| Z | 4 |
| Q _{calc} g/cm ³ | 1.295 |
| μ/mm ⁻¹ | 0.855 |
| F(000) | 1756.0 |
| Crystal size/mm ³ | 0.485 × 0.236 × 0.19 |
| Radiation | MoKα ($\lambda = 0.71073$) |
| 2Θ range for data collection/° | 2.388 to 52.766 |
| Index ranges | -20 ≤ h ≤ 20, -20 ≤ k ≤ 18, -21 ≤ l ≤ 21 |
| Reflections collected | 65896 |
| Independent reflections | 4494 [$R_{\text{int}} = 0.0430$, $R_{\text{sigma}} = 0.0189$] |
| Data/restraints/parameters | 4494/11/285 |
| Goodness-of-fit on F ² | 1.337 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0750$, $wR_2 = 0.1798$ |
| Final R indexes [all data] | $R_1 = 0.0759$, $wR_2 = 0.1823$ |
| Largest diff. peak/hole / e Å ⁻³ | 0.69/-1.19 |
| Flack parameter | 0.008(4) |

Table S2. Bond lengths of M-N.

| | Bond length (\AA) |
|-------|------------------------------|
| M-N1 | 2.12 (1) |
| M-N4 | 2.12(1) |
| M-N7 | 2.13(1) |
| M-N8 | 2.07(1) |
| M-N11 | 2.12(1) |
| M-N12 | 2.06(1) |

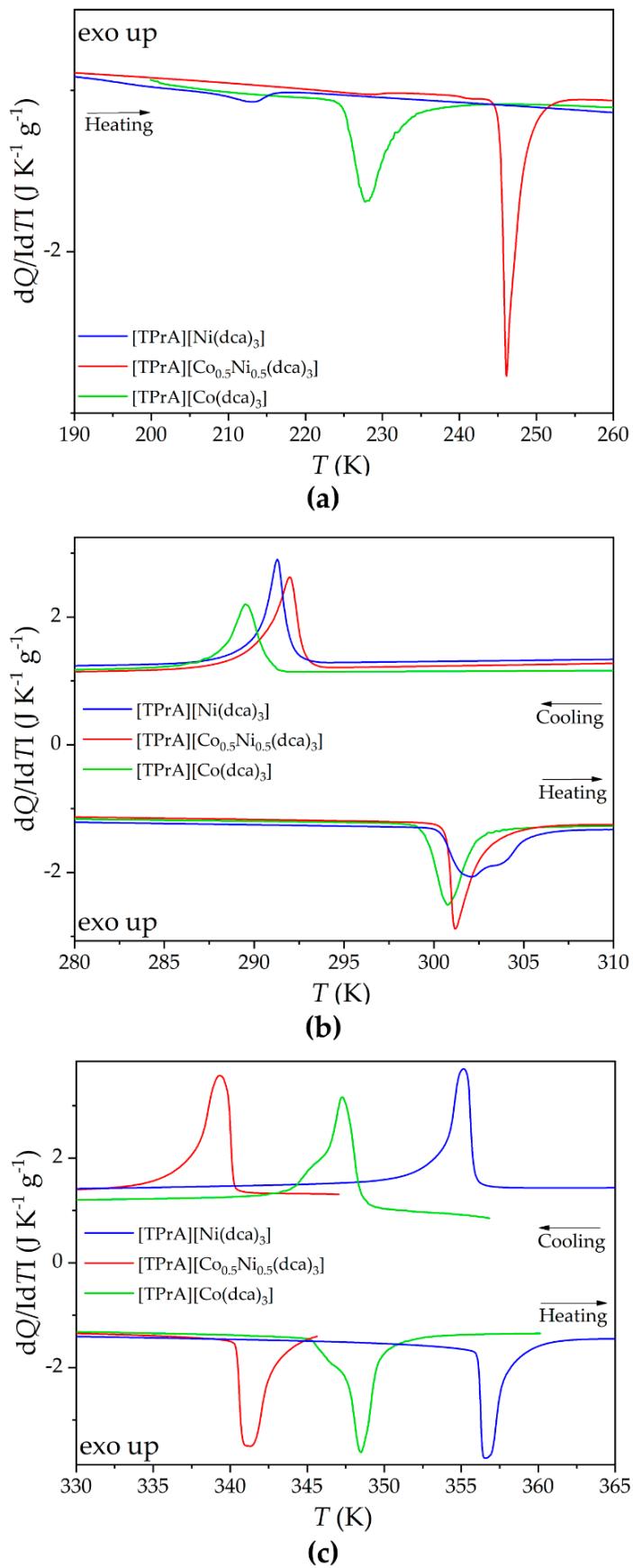


Figure S5. Detail of the DSC of the [TPrA][Co(dca)₃], [TPrA][Co_{0.5}Ni_{0.5}(dca)₃] and [TPrA][Ni(dca)₃] from (a) 200 K to 260 K, (b) 280 K to 310 K and (c) 330 K to 365 K.

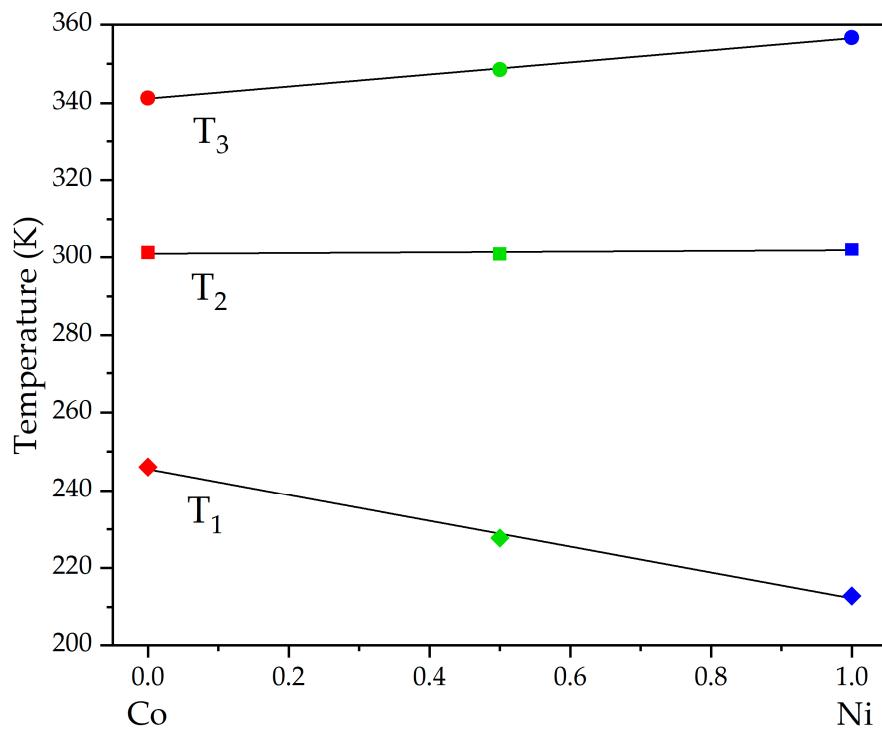


Figure S6. Dependence of the transition temperature observed by DSC (by heating) on the metal proportion, for the samples [TPrA][Co(dca)₃], [TPrA][Co_{0.5}Ni_{0.5}(dca)₃] and [TPrA][Ni(dca)₃].

Table S3. UV-Vis bands of the [TPrA][Co_xNi_{1-x}(dca)₃] ($x = 1.0, 0.5, 0.0$).

| Co(II) ground state $^4\text{T}_1(\text{F})$ | λ (nm) | |
|--|----------------------------------|---|
| $^4\text{T}_1(\text{P})$ | 484 | Intense and wide band. Overlapping with $^2\text{T}_2(\text{G})$ band |
| $^2\text{T}_2(\text{G})$ | 523 | Intense and wide band. Overlapping with $^4\text{T}_1(\text{P})$ band |
| ^2E , $^2\text{T}_1(\text{G})$ | 613 | Weak band. Overlapping and partially concealed by previous signals. |
| Ni(II) ground state $^3\text{A}_{2g}(\text{F})$ | λ (nm) | |
| $^3\text{T}_{1g}(\text{P})$ | 388 and 458 | Intense narrow band with a shoulder (symmetry loss) |
| $^4\text{T}_{1g}(\text{F})$ | 635 and 723 | Intense wide band with a shoulder (symmetry loss) |
| Ni(II) + Co(II) solid solution ground states $^4\text{T}_1(\text{F})$ (from Co(II)) and $^3\text{A}_{2g}(\text{F})$ (from Ni(II)) | λ (nm) | |
| $^3\text{T}_{1g}(\text{P})$ | 388 | Intense narrow band |
| $^4\text{T}_1(\text{P})$ | 480 | Intense and wide band. Overlapping with $^2\text{T}_2(\text{G})$ band |
| $^2\text{T}_2(\text{G})$ | 518 | Intense and wide band. Overlapping with $^4\text{T}_1(\text{P})$ band |
| $^4\text{T}_{1g}(\text{F})$ | 630 and 723 | Intense wide band with a shoulder (symmetry loss) |

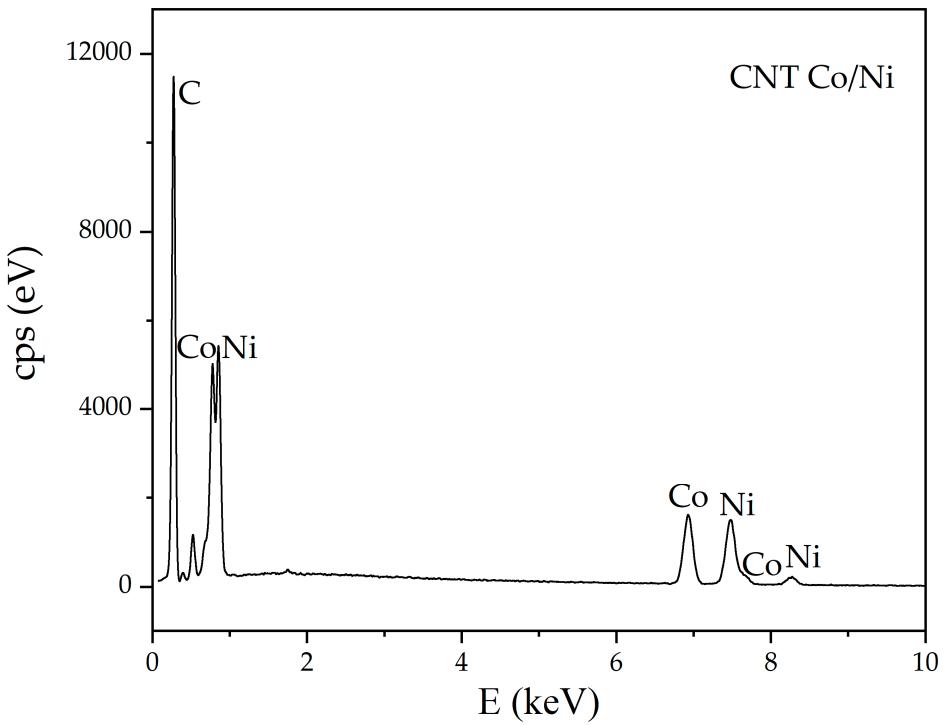


Figure S7. EDS spectrum of the CNTs obtained with the calcination of [TPrA][Co_{0.5}Ni_{0.5}(dca)₃].