# Supplementary Information

# A new series of magnetic and luminescent layered hybrid materials obtained from thianthrene phosphonic acid: $M(H_2O)PO_3$-$S_2C_{12}H_7$ (M = Cu, Zn) and $M(H_2O)_2(PO_2OH$-$S_2C_{12}H_7)_2$ (M = Mn, Co)

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Keywords: Hybrid materials, metallophosphonate, layered structure, magnetism, luminescence.

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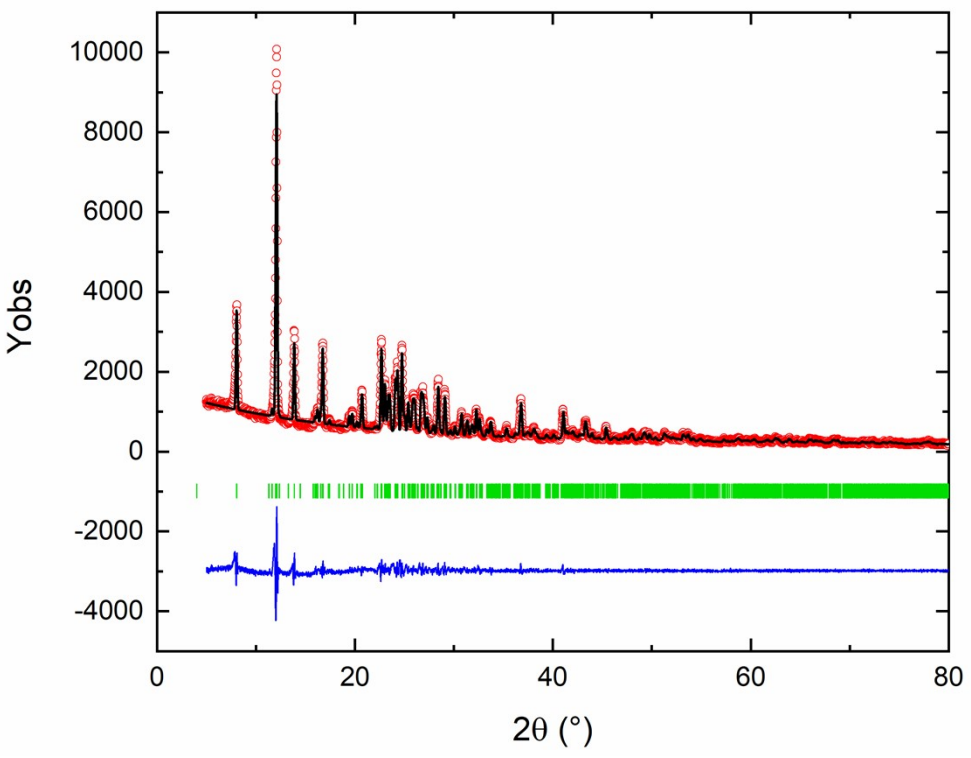
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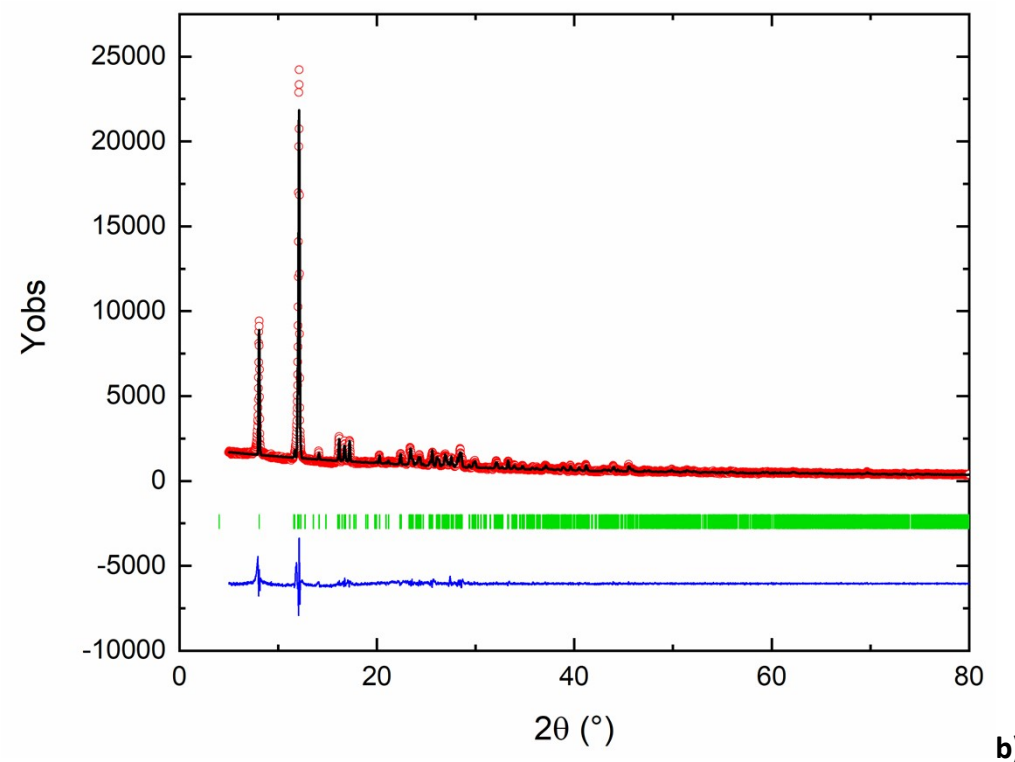
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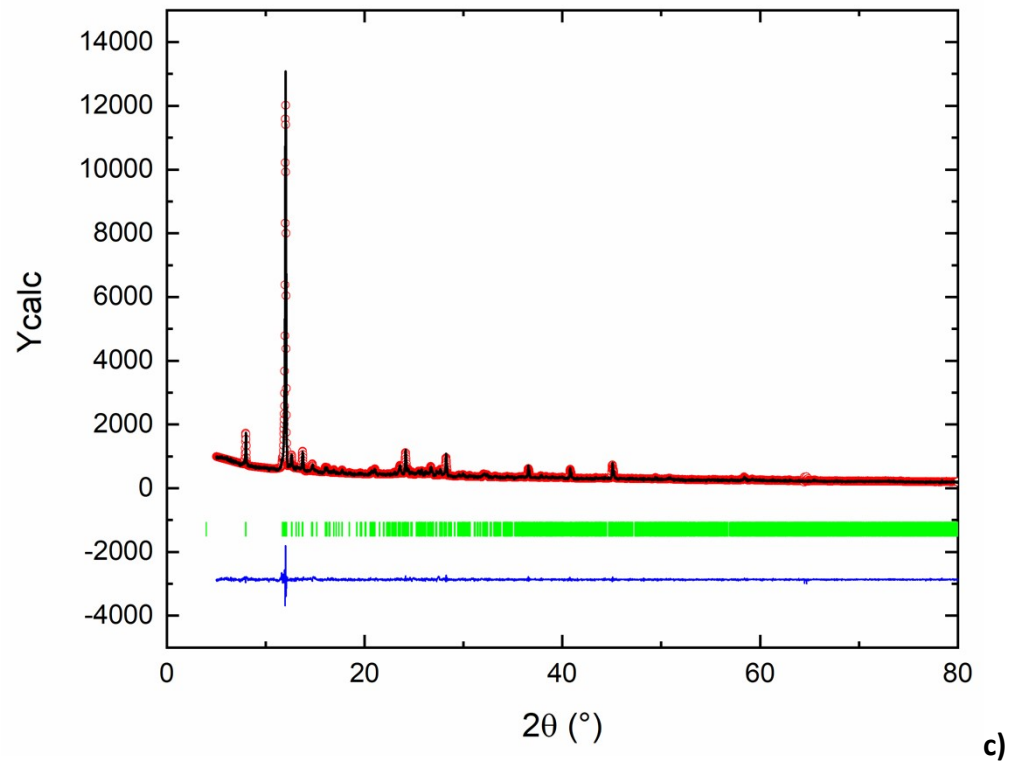


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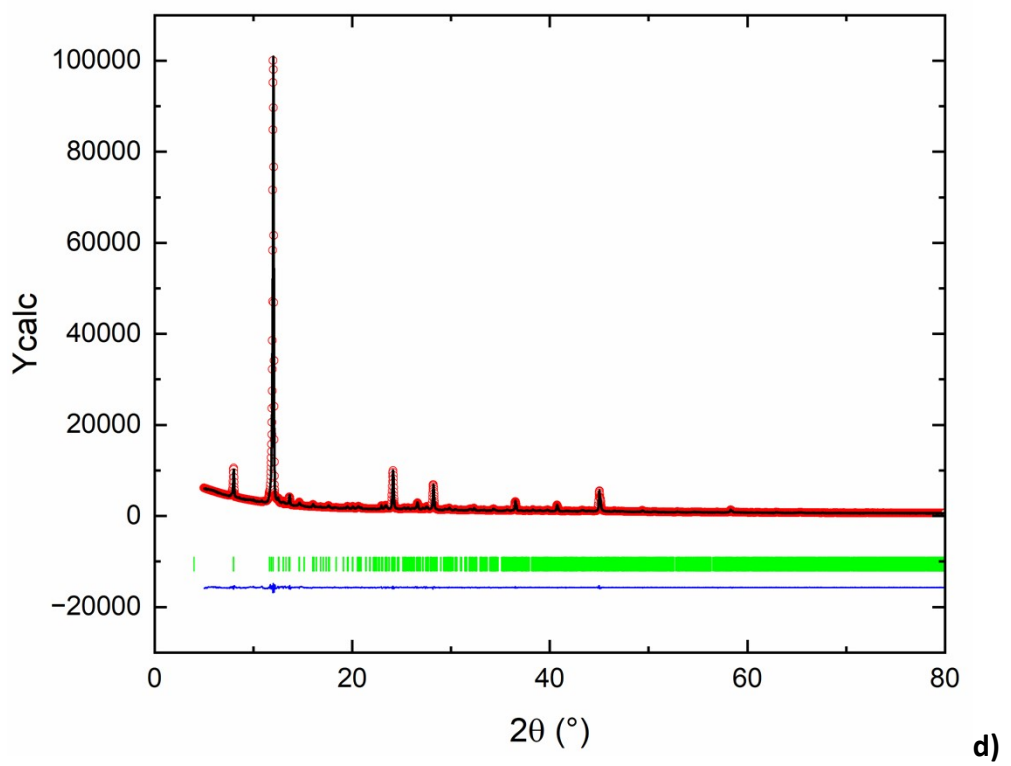
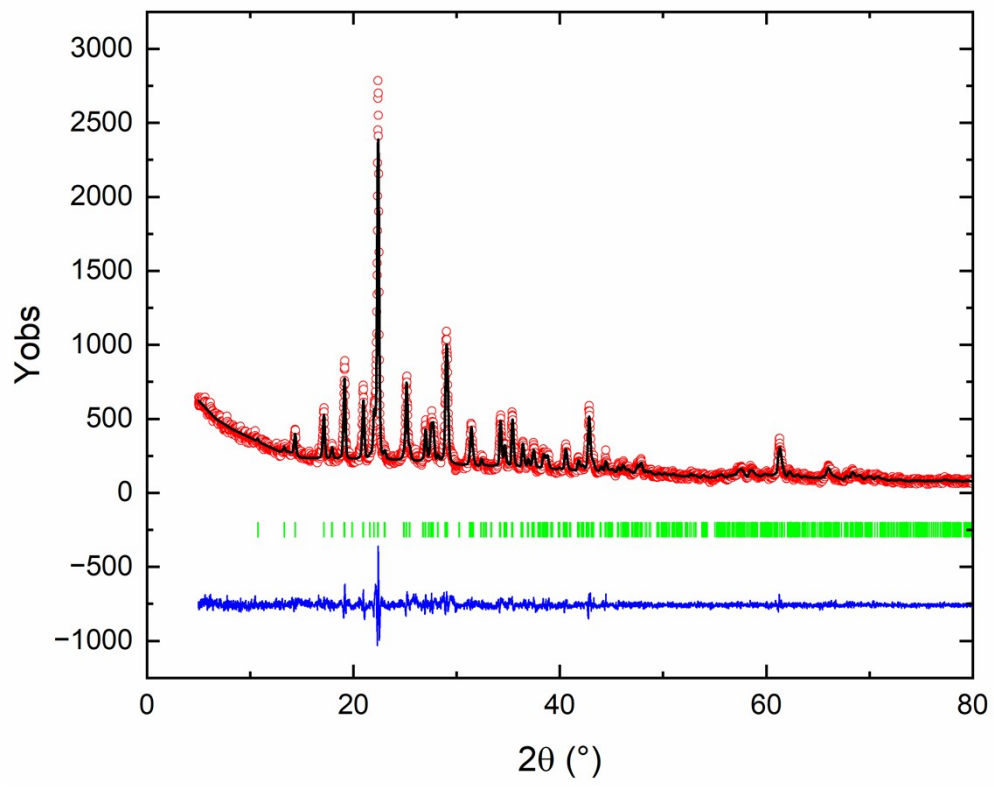



**d)**

FIGURE SI 1 : Powder X ray diffraction recorded on compounds a) $Zn(H_2O)(PO_3S_2C_{12}H_7)$ **(4)**; b) $Cu(H_2O)(PO_3S_2C_{12}H_7)$ **(5)**, c) $Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(6)** and d) $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(7)**. Experimental diagram (red circles), calculated position of the peaks (green dashes), calculated pattern from the single cif file (black line), difference between experimental and calculated pattern (blue line)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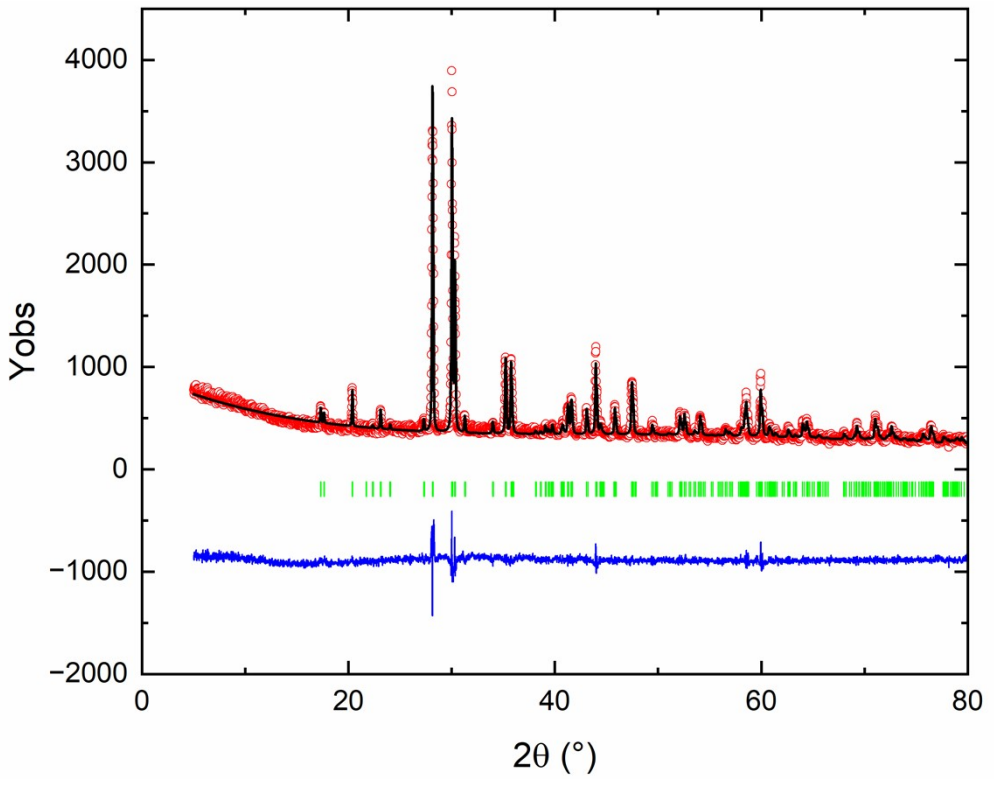
**a)**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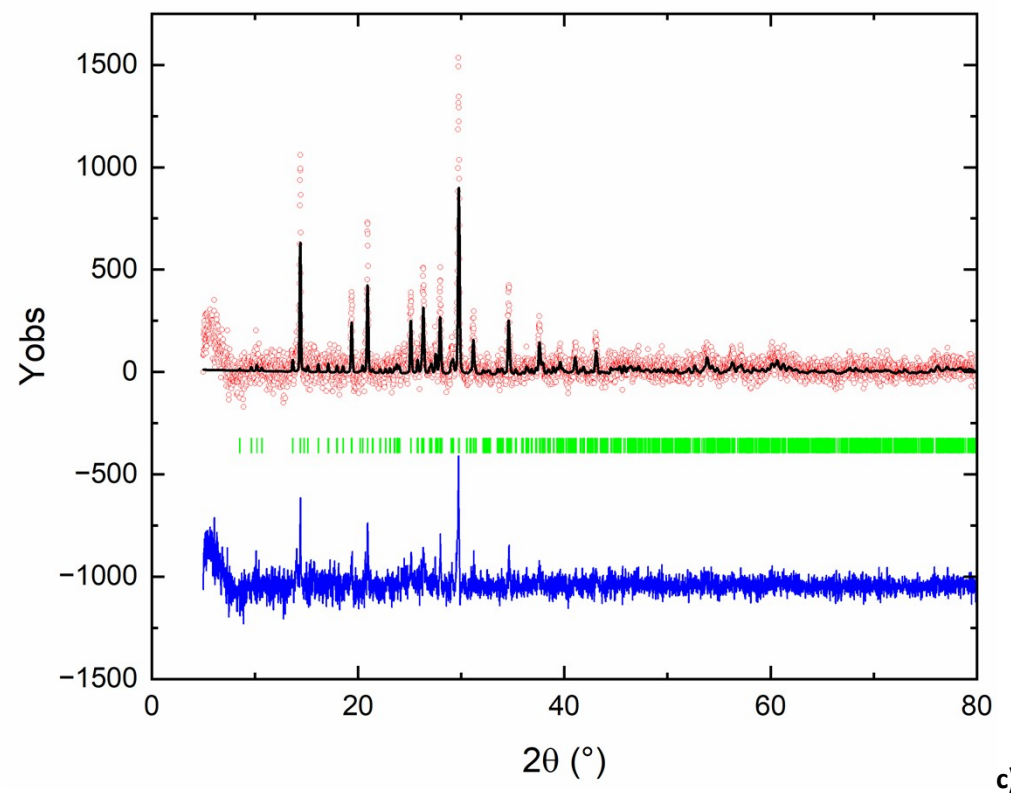


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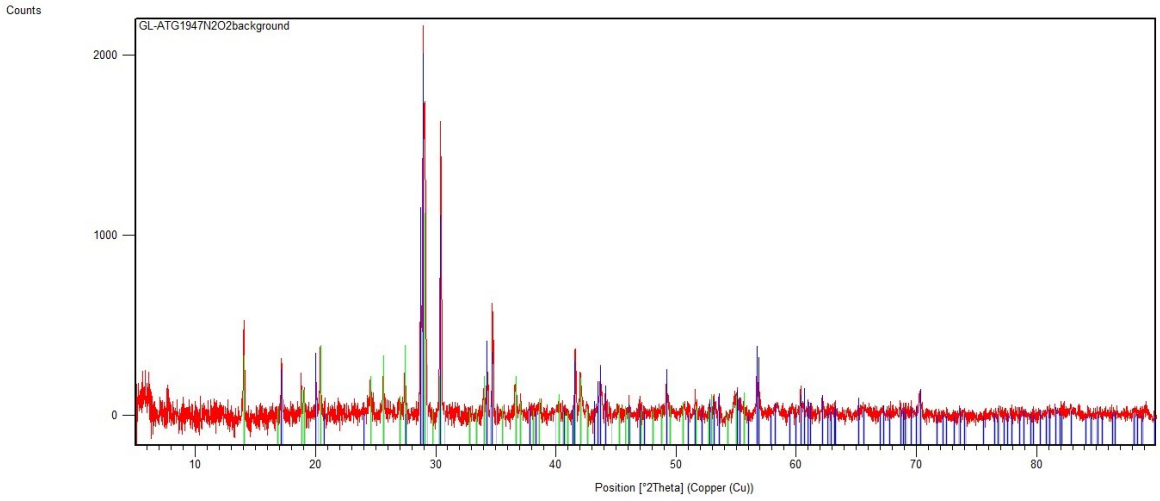



**d**)

FIGURE SI 2 : X-ray diffraction pattern of the decomposition products of the four hybrid materials (a) $Zn_2P_2O_7$ (b) $Cu_2P_2O_7$ (c) $CoP_2O_6$ and (d) a mix of $Mn_2P_2O_7$ (blue) and $MnP_2O_6$ (green)

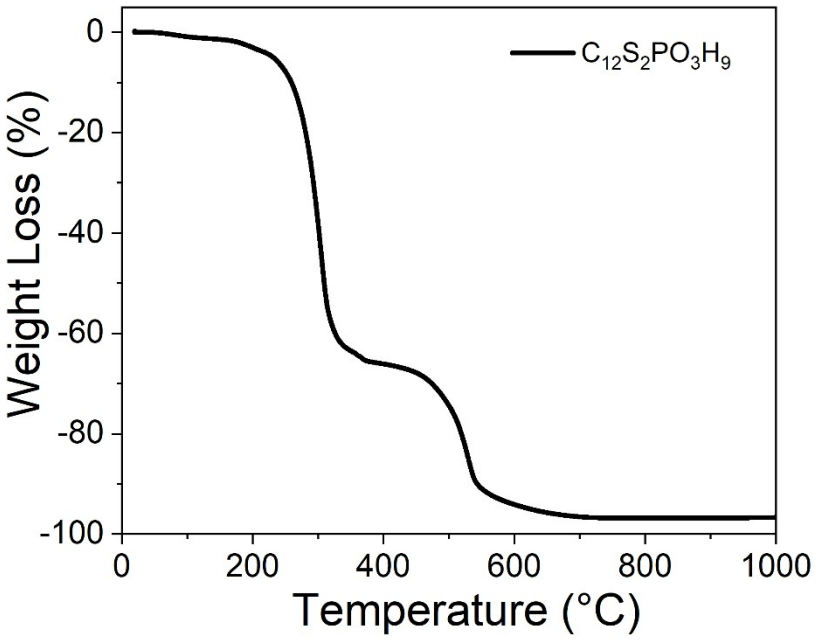



FIGURE SI 3 : thermogravimetric curve of $PO(OH)_2S_2C_{12}H_7$ **(3)**

| **O•••H-O hydrogen bonds between the phosphonic acid functions of $PO(OH)_2S_2C_{12}H_7$ (blue dashed lines)** | | | |
|---|---|---|---|
| O16-H16•••O18 | 3.2623(17) Å | O18-H18•••O16 | 3.180(2) Å |
| O18-H18•••O18 | 3.217(2) Å | O18-H18•••O18 | 3.165(2) Å |
| O18-H18•••O17 | 1.7999(17) Å | O16-H16•••O17 | 1.834(2) Å |
| **C•••H-C interaction between the $C_6H_4$ rings of $PO(OH)_2S_2C_{12}H_7$ in one layer (light green dashed lines)** | | | |
| C5-H5•••C4 | 3.158(3) Å | C5-H5•••C5 | 2.813(4) Å |
| C5-H5•••C6 | 3.160(4) Å | | |
| **C•••H-C interaction between two adjacent layers (dark green dashed lines)** | | | |
| C11-H11•••C10 | 3.299(3) Å | C11-H11•••C8 | 3.285(3) Å |
| C12-H12•••C6 | 2.970(3) Å | C7-H7•••C12 | 3.205(3) Å |
| C12-H12•••C7 | 2.709(4) Å | | |
| **S•••H-C interaction between two adjacent layer (pink dashed lines)** | | | |
| C14-H14•••S2 | 2.9836(8) Å | C11-H11•••S9 | 3.2007(8) Å |

Table SI 1 : Intermolecular: i) O•••H-O hydrogen bonds ranging from 1.8 to 3.3 Å; ii) C•••H-C interactions ranging from 2.7 to 3.3 Å; iii) S•••H-C interactions ranging from 2.9 to 3.4 Å.

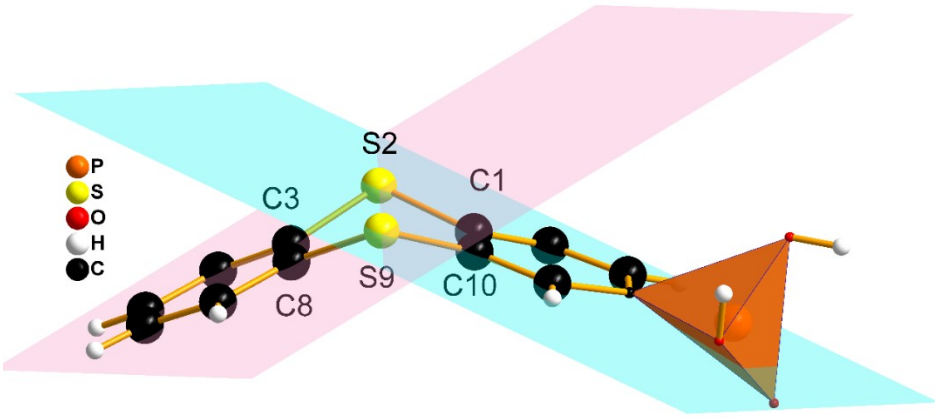



FIGURE SI 4: Chemical structure of 3-thianthrenephosphonic acid precursor.

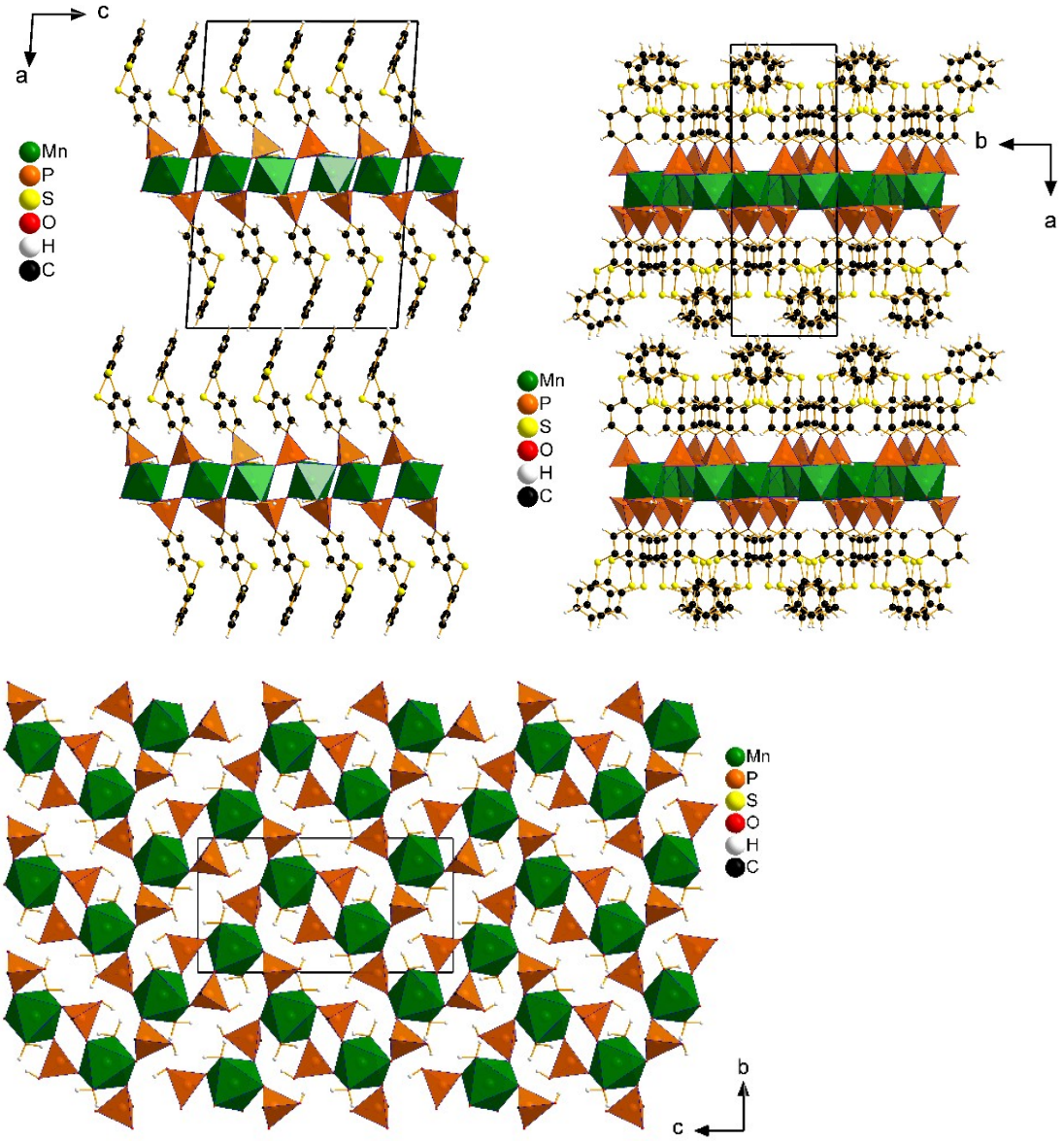



FIGURE SI 5 : View of the lamellar structure of $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(7).**

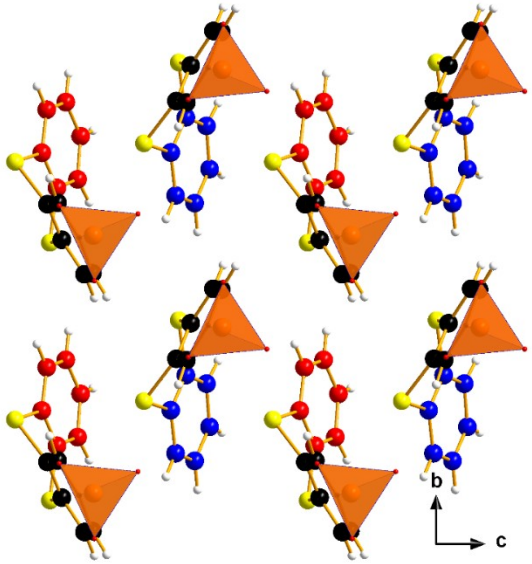



FIGURE SI 6 View of the orientation of the $C_6H_4$ ring along the b and -b direction of $Zn(H_2O)(PO_3S_2C_{12}H_7)$ **(4)** also present in $Cu(H_2O)(PO_3S_2C_{12}H_7)$ **(5)**.

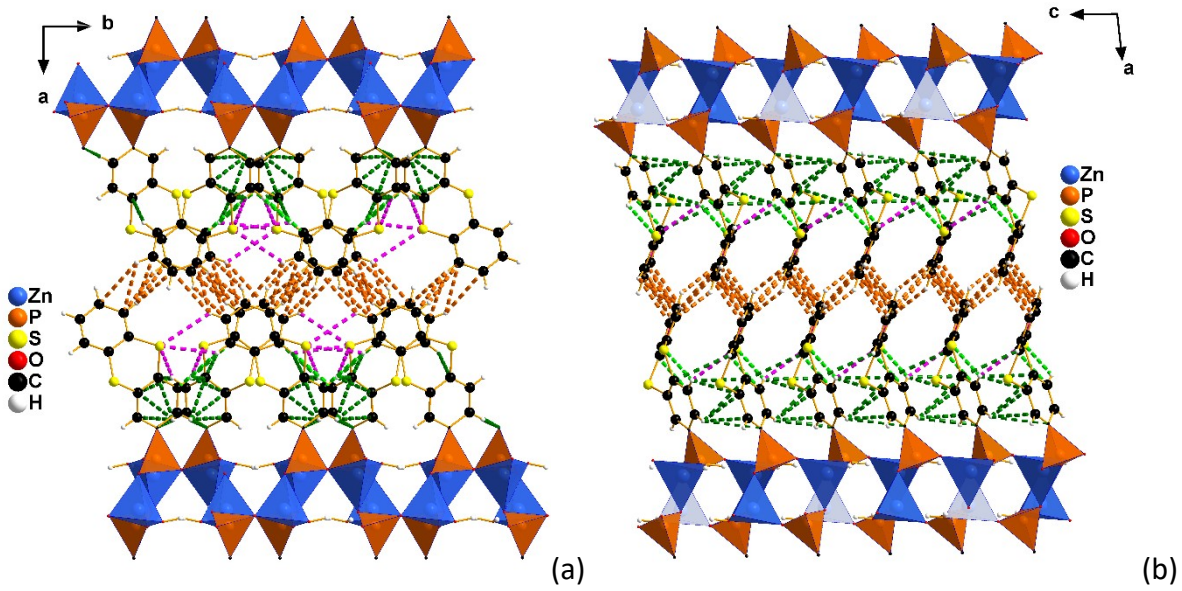



FIGURE SI 7: (a) Representation of the C•••H-C (light and green dashed lines) and S•••H-C (pink dashed lines) interactions in the structure of $Zn(H_2O)(PO_3S_2C_{12}H_7)$ **(4)** (a) view along the c direction; (b) view along the b direction.

| C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of $Zn(H_2O)(PO_3S_2C_{12}H_7)$ (4) in one column (light green dashed lines) | | | |
|---|---|---|---|
| C8-H8•••C5 | 3.258(4) Å | C5-H5•••C8 | 3.263(5) Å |
| **C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (4) in two adjacent columns (dark green dashed lines)** | | | |
| C6-H6•••C1 | 3.283(4) Å | C6-H6•••C2 | 3.099(4) Å |
| C5-H5•••C3 | 3.278(4) Å | C6-H6•••C3 | 3.097(4) Å |
| C5-H5•••C4 | 3.045(4) Å | C8-H8•••C4 | 3.395(4) Å |
| C6-H6•••C4 | 3.351(3) Å | | |
| **C•••H-C interaction between two adjacent organic layers of (4) (orange dashed lines)** | | | |
| C11-H11•••C10 | 3.259(5) Å | C10-H10•••C9 | 3.283(5) Å |
| C11-H11•••C11 | 3.310(4) Å | C11-H11•••C9 | 3.113(5) Å |
| C9-H9•••C11 | 3.127(4) Å | C9-H9•••C10 | 3.343(5) Å |
| **S•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (4) (pink dashed lines)** | | | |
| C9-H9•••S1 | 3.2446(10) Å | C8-H8•••S1 | 3.1232(10) Å |
| C5-H5•••S1 | 3.0354(10) Å | | |

Table SI 2 Intermolecular: i) C•••H-C interactions between 2.7 to 3.4 Å; ii) S•••H-C interactions between 2.9 to 3.4 Å.

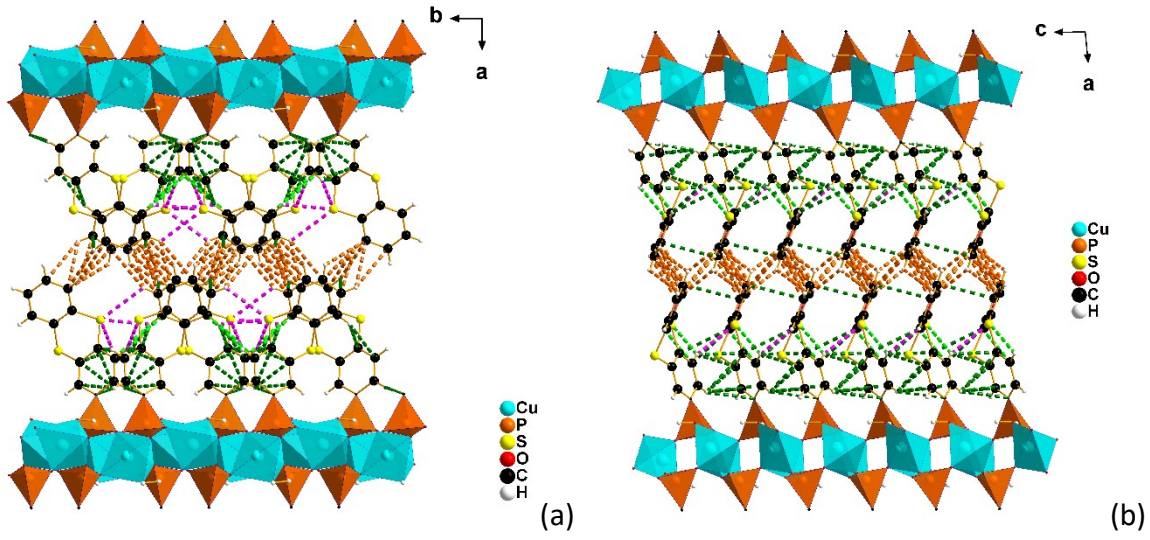
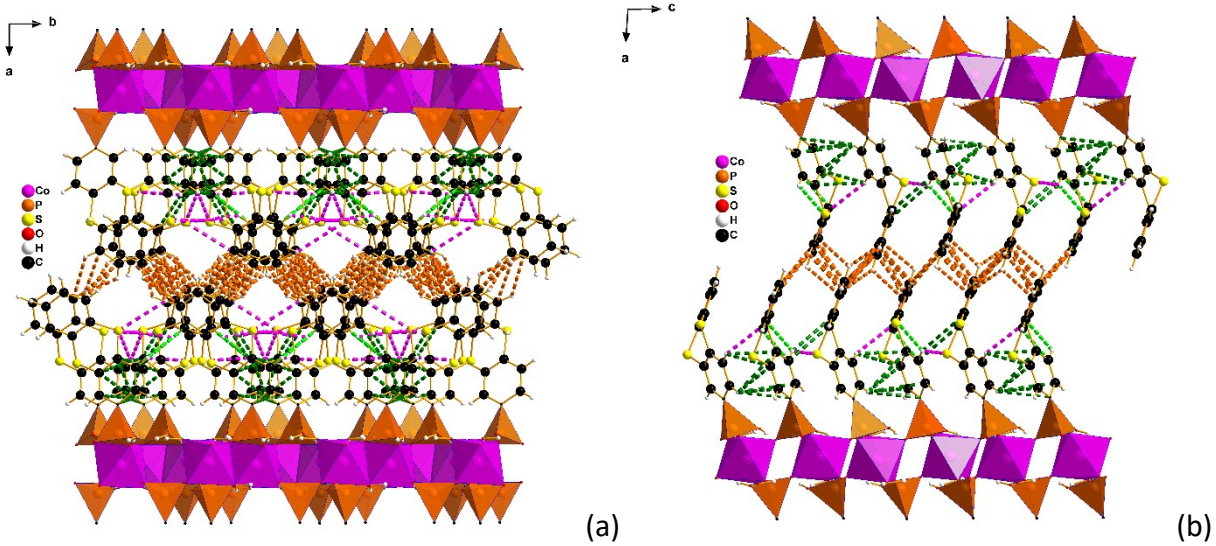



FIGURE SI 8 : (a) Representation of the C•••H-C (light and green dashed lines) and S•••H-C (pink dashed lines) interactions in the structure of $Cu(H_2O)(PO_3S_2C_{12}H_7)$ **(5)** (a) view along the c direction; (b) view along the b direction.

| C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of $Cu(H_2O)(PO_3S_2C_{12}H_7)$ (5) in one column (light green dashed lines) | | | |
|---|---|---|---|
| C11-H11•••C3 | 3.304 (5) Å | C3-H3•••C11 | 3.348 (5) Å |
| **C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (5) in two adjacent columns (dark green dashed lines)** | | | |
| C8-H8•••C10 | 3.270 (6) Å | C2-H2•••C5 | 3.069 (4) Å |
| C3-H3•••C4 | 2.856 (4) Å | C11-H11•••C4 | 3.291 (4) Å |
| C2-H2•••C2 | 3.288 (5) Å | C2-H2•••C1 | 3.056 (4) Å |
| C2-H2•••C6 | 2.949 (5) Å | C3-H3•••C5 | 3.075 (4) Å |
| C2-H2•••C4 | 3.304 (4) Å | C11-H11•••C3 | 3.300 (5) Å |
| **C•••H-C interaction between two adjacent organic layers of (5) (orange dashed lines)** | | | |
| C10-H10•••C9 | 3.255 (6) Å | C10-H10•••C8 | 3.114 (5) Å |
| C8-H8•••C9 | 3.203 (6) Å | C8-H8•••C10 | 3.094 (5) Å |
| C9-H9•••C10 | 3.243 (6) Å | C9-H9•••C8 | 3.388 (5) Å |
| C8-H8•••C8 | 3.341 (5) Å | | |
| **S•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (5) (pink dashed lines)** | | | |
| C10-H10•••S1 | 3.1677 (12) Å | C11-H11•••S1 | 2.9494 (12) Å |
| C3-H3•••S1 | 2.9395 (11) Å | | |

Table SI 3 : Intermolecular: i) C•••H-C interaction between 2.7 to 3.4 Å; ii) S•••H-C interaction between 2.9 to 3.4 Å.




(a) (b)

FIGURE SI 9: (a) Representation of the C•••H-C (light and green dashed lines) and S•••H-C (pink dashed lines) interactions in the structure of $Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ (6) (a) view along the c direction; (b) view along the b direction.

| C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of $Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ (6) in one column (light green dashed lines) | | | |
|---|---|---|---|
| C20-H20•••C17 | 3.18(1) Å | C17-H17•••C20 | 3.20(2) Å |
| **C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (6) in two adjacent columns (dark green dashed lines)** | | | |
| C6-H6•••C13 | 3.165(8) Å | C6-H6•••C14 | 3.062(8) Å |
| C5-H5•••C16 | 3.001(8) Å | C6-H6•••C18 | 3.37(1) Å |
| C6-H6•••C16 | 3.341(9) Å | C5-H5•••C15 | 3.240(8) Å |
| C6-H6•••C15 | 3.118(8) Å | C17-H17•••C8 | 3.32(1) Å |
| C8-H8•••C17 | 3.36(1) Å | | |
| **C•••H-C interaction between two adjacent organic layers of (6) (orange dashed lines)** | | | |
| C10-H10•••C11 | 3.36(2) Å | C22-H22•••C9 | 3.21(2)Å |
| C11-H11•••C23 | 3.18(1) Å | C11-H11•••C9 | 3.23(2) Å |
| C9-H9•••C11 | 3.39(1) Å | C11-H11•••C10 | 3.09(2) Å |
| C23-H23•••C11 | 3.19(1) Å | C10-H10•••C21 | 3.25(2) Å |
| C23-H23•••C23 | 2.96(1) Å | C23-H23•••C22 | 3.14(2) Å |
| C9-H9•••C22 | 3.03(2) Å | C9-H9•••C21 | 3.24(2)Å |
| C21-H21•••C10 | 3.05(2) Å | C21-H21•••C9 | 3.25(2) Å |
| **S•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (6) (pink dashed lines)** | | | |
| C17-H17•••S1 | 3.102(3) Å | C21-H21•••S4 | 3.317(3) Å |
| C5-H5•••S4 | 2.995(3) Å | C8-H8•••S2 | 3.159(3) Å |
| C20-H20•••S4 | 3.207(3) Å | | |

Table SI 4 : Intermolecular: i) C•••H-C interaction between 2.7 to 3.4 Å; ii) S•••H-C interaction between 2.9 to 3.4 Å for $Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ (**6**).

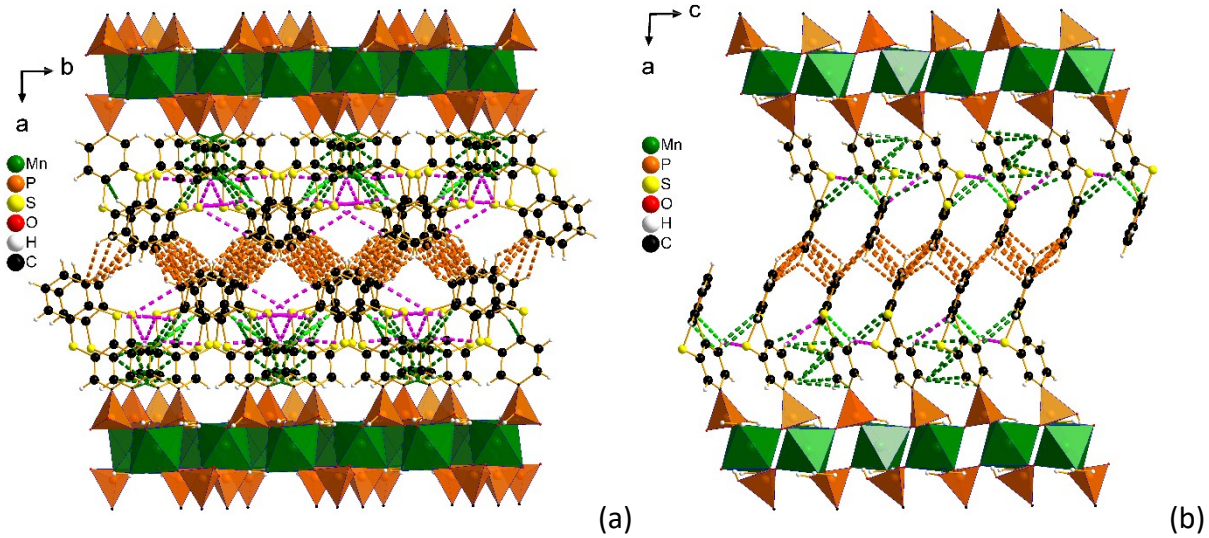



FIGURE SI 10 : (a) Representation of the C•••H-C (light and green dashed lines) and S•••H-C (pink dashed lines) interactions in the structure of $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(7)** (a) view along the c direction; (b) view along the b direction.

| C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ (7) in one column (light green dashed lines) | | | |
|---|---|---|---|
| C14-H14•••C24 | 3.233(3) Å | C24-H24•••C14 | 3.247(4) Å |
| **C•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (7) in two adjacent columns (dark green dashed lines)** | | | |
| C7-H7•••C19 | 3.008 (3) Å | C8-H8•••C19 | 3.369 (3) Å |
| C14-H14•••C2 | 3.375 (3) Å | C24-H24•••C9 | 3.302 (3) Å |
| C24-H24•••C14 | 3.247 (4) Å | C7-H7•••C20 | 3.269 (3) Å |
| C9-H9•••C24 | 3.353 (3) Å | C8-H8•••C22 | 3.208 (2) Å |
| **C•••H-C interaction between two adjacent organic layers of (7) (orange dashed lines)** | | | |
| C8-H8•••C21 | 3.105 (3) Å | C8-H8•••C20 | 3.155 (3) Å |
| C17-H17•••C17 | 2.971 (3) Å | C10-H10•••C16 | 3.035 (4) Å |
| C15-H15•••C11 | 3.081 (4) Å | C12-H12•••C11 | 3.096 (4) Å |
| C17-H17•••C12 | 3.163 (3) Å | C17-H17•••C16 | 3.181 (4) Å |
| C10-H10•••C15 | 3.249 (4) Å | C11-H11•••C15 | 3.277 (4) Å |
| C15-H15•••C10 | 3.281 (3) Å | C11-H11•••C12 | 3.367 (4) Å |
| C10-H10•••C12 | 3.391 (3) Å | C16-H16•••C10 | 3.224(3) |
| C12-H12•••C10 | 3.229(4) Å | C12-H12•••C17 | 3.163 (3) Å |
| **S•••H-C interaction between the $PO_3S_2C_{12}H_9$ moieties of (7) (pink dashed lines)** | | | |
| C7-H7•••S4 | 3.0047 (7) Å | C24-H24•••S1 | 3.1634 (6) Å |
| C15-H15•••S4 | 3.3384 (7) Å | C14-H14•••S4 | 3.3044 (7) Å |
| C9-H9•••S2 | 3.2463 (6) Å | | |

Table SI 5 : Intermolecular: i) C•••H-C interaction between 2.7 to 3.4 Å; ii) S•••H-C interaction between 2.9 to 3.4 Å for $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(7)**.

Table A1: Tabulated the peak fitting information of Absorbance with Gaussian function

| **Compounds** | | **Energy (eV)** | **Wavelength (nm)** | **Reduced chi²** | **FWHM** |
|---|---|---|---|---|---|
| $PO(OH)_2S_2C_{12}H_7$ **(3)** | AI | 4.58 | 270 | 1.10765E-4 | 1.49406 |
| | AII | 3.71 | 333 | | 0.61949 |
| | AIII | 3.40 | 364 | | 0.32972 |
| | AIV | 2.44 | 506 | | 0.93805 |
| *$Zn(H_2O)(PO_3S_2C_{12}H_7)$* ***(4)*** | AI | 4.66 | 265 | 1.52964E-4 | 1.45058 |
| | AII | 3.76 | 329 | | 0.55431 |
| | AIV | 2.89 | 429 | | 1.49267 |
| *$Cu(H_2O)(PO_3S_2C_{12}H_7)$* ***(5)*** | AI | 4.72 | 262 | 1.12961E-4 | 1.49879 |
| | AII | 3.70 | 334 | | 0.68241 |
| | AIII | 3.07 | 403 | | 0.72344 |
| | AIV | 1.66 | 742 | | 0.41236 |
| *$Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$* ***(6)*** | AI | 4.71 | 262 | 7.92081E-5 | 1.18879 |
| | AII | 3.72 | 333 | | 0.79531 |
| | AIII | 3.44 | 360 | | 0.27453 |
| | AIV | 2.75 | 450 | | 0.6635 |
| | AV | 2.34 | 528 | | 0.5312 |

| | | | | | |
|---|---|---|---|---|---|
| $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ ***(7)*** | AI | 4.60 | 269 | 3.06447E-5 | 1.2357 |
| | AII | 3.80 | 325 | | 0.62495 |
| | AIII | 3.51 | 352 | | 0.34333 |
| | AIV | 2.96 | 418 | | 2.13826 |

Table A2: Tabulated the peak fitting information of photoluminescence with Gaussian function

| **Compounds** | | **Energy (eV)** | **Wavelength (nm)** | **Reduced chi²** | **FWHM** |
|---|---|---|---|---|---|
| $PO(OH)_2S_2C_{12}H_7$ **(3)** | LIII | 2.92 | 425 | 3.91115E-6 | 0.54649 |
| | LIV | 2.47 | 501 | | 0.29712 |
| $Zn(H_2O)(PO_3S_2C_{12}H_7)$ **(4)** | LIII | 2.99 | 414 | 2.61976E-7 | 0.29879 |
| | LIV | 2.46 | 503 | | 0.88208 |
| | LV | 1.82 | 681 | | 0.29341 |
| $Cu(H_2O)(PO_3S_2C_{12}H_7)$ **(5)** | LI | 3.97 | 312 | 4.09451E-9 | 0.64828 |
| | LIII | 2.95 | 420 | | 0.35654 |
| | LIV | 2.39 | 518 | | 0.53454 |
| | LV | 1.97 | 627 | | 1.30235 |
| $Co(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(6)** | LI | 3.61 | 343 | 2.49327E-9 | 0.12156 |
| | LII | 3.40 | 364 | | 0.13526 |
| | LIII | 2.98 | 415 | | 0.42864 |
| | LIV | 2.43 | 510 | | 0.41104 |
| | LV | 2.00 | 610 | | 0.42307 |
| $Mn(H_2O)_2(PO_2OHS_2C_{12}H_7)_2$ **(7)** | LIII | 2.98 | 414 | 3.42801E-8 | 0.29525 |
| | LIV | 2.46 | 502 | | 0.92081 |
| | LV | 1.93 | 642 | | 0.4988 |

Table SI 6 : Absorbance (Table A1) and photoluminescence (Table A2) peak fitting information with a Gaussian function.

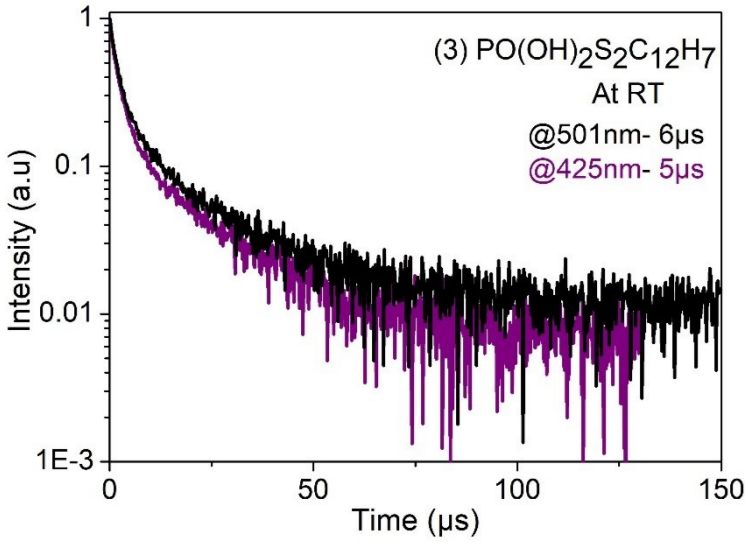



FIGURE SI 11: Thianthrene phosphonic acid $PO(OH)_2S_2C_{12}H_7$ **(3)** decay time at 425 nm **(LIII)** (black) and 501 nm **(LIV)** (Purple) under 266 nm excitation wavelength performed at room temperature.