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Electronic Supporting Information for:

Intrinsic Dual-Emitting Gold Thiolate Coordination Polymer, [Au(+I)(*p*-SPhCO₂H)]_n, for Ratiometric Temperature Sensing

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Experiments and methods

Routine X-ray diffraction (XRD) was carried out on a Bruker D8 Advance A25 diffractometer using Cu K α radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). XR scattering was recorded between 4° and 90° (2 θ) with 0.02° steps and 0.5 s per step (28 min for the scan). Divergence slit was fixed to 0.2° and the detector aperture to 189 channels (2.9°).

The structural determination of [Au(p-SPhCO₂H)]_n was carried out from X-ray powder diffraction data from a highly crystalline compound synthesized at 180 °C and mixed with bulk gold (Fig. S1 and S2). Sample was introduced into a 0.5 mm capillary and spun during data collection to ensure good powder averaging. The pattern was scanned at room temperature on a Bruker D8 Advance diffractometer with a Debye-Scherrer geometry, in the 2θ range 2-100°. The D8 system is equipped with a Ge(111) monochromator producing Cu $K\alpha_1$ radiation ($\lambda =$ 1.540598 Å) and a LynxEye detector. All calculations of structural investigation were performed with the TOPAS program.¹ The LSI-indexing method converged unambiguously to a triclinic unit cell. Unindexed lines observed on the powder pattern correspond to bulk gold. Given the small number of lines, the presence of gold did not prevent us to solve the structure. Indeed, at this stage the structural model of gold was taken into account and its contribution can be calculated by using the Rietveld method. The quantitative amount of bulk gold was estimated to be about 22 wt%. Structural investigation of [Au(p-SPhCO₂H)]_n was initialized by using the charge flipping method, which allowed location of gold atoms. The direct space strategy was then used to complete the structural models and organic moieties have been added to the fixed gold atomic coordinates and treated as rigid bodies in the simulated annealing process. The final Rietveld plot (Fig. S2) corresponds to satisfactory model indicator and profile factors (Table S1: $R_B = 0.031$ and $R_{wp} = 0.070$). CCDC-1539671 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Thermo-gravimetric analysis (TGA) were performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 2 mg of sample was heated at a rate of 10 °C.min⁻¹, in a 70 μ L alumina crucible, under air or nitrogen atmosphere (20 mL.min⁻¹). Shining droplets of bulk gold were observed at the end of experiment.

The infrared spectra were obtained from a Bruker Vector 22 FT-IR spectrometer with KBr pellets at room temperature and registered from 4000 cm⁻¹ to 400 cm⁻¹.

Sulphur percentage is determined by full combustion at 1320-1360 °C under O_2 stream and analysis of SO_2 and is titrated in a coulometric-acidimetric cell. Carbon and hydrogen percentages are determined by full combustion at 1030-1070 °C under O_2 stream and transformed into CO_2 and H_2O and are titrated on a coulometric detector. Analysis precision is 0.3% absolute for carbon, sulphur and hydrogen.

SEM images were obtained with FEI Quanta 250 FEG scanning electron microscope, samples were mounted on stainless pads and sputtered with Au/Pd alloy to prevent charging during observation.

X-ray photoelectron spectroscopy (XPS) experiment was carried out on a KRATOS Axis Ultra DLD spectrometer using monochromated Al K α source (hv = 1486.6 eV, 150 W), a pass energy of 20 eV, a hybrid lens mode and an indium sample holder in ultra-high vacuum ($P < 10^{-9}$ mbar). The analyzed surface area was 300 µm × 700 µm. Charge neutralization was required for all samples. Scan survey was done at an energy of 160 ev and the elements Au 4f, S 2p and C 1s at 20 eV. The peaks (Au 4f, S 2p) were referenced to the aromatic carbon atoms components of the C 1s band at 284.7 eV. Shirley background subtraction and peak decomposition using Gaussian–Lorentzian products were performed with the Vision 2.2.6 Kratos processing program.

The photoluminescence was performed on a homemade apparatus. The sample was illuminated by a EQ99X laser driven light source filtered by a Jobin Yvon Gemini 180 monochromator. The exit slit from the monochromator was then reimaged on the sample by two 100m focal length, 2 inch diameter MgF_2 lenses. The whole apparatus has been calibrated by means of a Newport 918D Low power calibrated photodiode sensor over the range 190-1000 nm. The resolution of the system being 4 nm. The emitted light from the sample is collected by an optical fiber connected to a Jobin-Yvon TRIAX320 monochromator equipped with a cooled CCD detector. At the entrance of the monochromator different long pass filter can be chosen in order to eliminate the excitation light. The resolution of the detection system is 2 nm.

Luminescence lifetime measurements were performed with a R2949 photomultiplier tube from Hamamatsu with a 379nm picosecond (57ps) laser with frequency controller from Hamamatsu. Photon arrival times were recorded by a MCS6A multichannel scaler from Fast ComTec. Temperature control over the sample was regulated with a THMS-600 heating stage with T95-PE temperature controller from Linkam Scientific Instruments. The collected data was fitted with a three-exponential function, yielding the individual luminescence lifetimes. The fastest lifetime (τ_3) was an unidentified component present in the measurement even without the sample (probably residual excitation pulse). While the two other lifetimes were linked to their respected emission peaks (τ_2 (fast component) – low energy and τ_1 (slow component) – high energy peak) with the time resolved spectroscopy measurements, the τ_3 was omitted from discussion for clarity. For time resolved spectroscopy measurements we used an USB Istar CCD from Andor (intensified charge coupled device) camera and a SR16 manual monochromator, calibrated with an Ar/Hg calibration lamp. The excitation setup the same as for the lifetime measurements. The delay after pulse (D) and the width (W) of the acquisition could be specified as well se the pulse frequency. Care was taken in ensuring that the frequency was low enough to allow for the full relaxation after each pulse to occur. Luminescence quantum yield was estimated by the same procedure as described previously.²

Au L₃-edge X-ray absorption fine structure (XAFS) data was collected from the CLS@APS (Sector 20-BM) beamline at the Advanced Photon Source (operating at 7.0 GeV) in Argonne National Labs, Chicago, IL, USA. [Au(p-SPhCO₂H)]_n and [Au(p-SPhCO₂Me)]_n samples were measured in transmission mode simultaneously with a gold foil reference at the Au L₃-edge (11.919 keV). Measurements were collected at room temperature and at 90 K using a liquid nitrogen cooled cryostat chamber. The amplitude reduction factor used for extended-XAFS (EXAFS) fitting was determined using a [Au(SC₁₂H₂₅)]_n polymer material. The Au-S coordination number (CN) was fixed at 2 to obtain a value of 0.93 which was used for all Au L₃-edge EXAFS fitting. EXAFS data was transformed and normalized into k- and R-space using the WinXAS program with conventional procedures. A k-range of 3.0-12.0 Å⁻¹ was used for all Fourier transforms of EXAFS spectra. Self-consistent multiple-scattering calculations were performed using the FEFF8.2 program to obtain scattering amplitudes and phase-shift functions used for fitting various scattering paths (Au-S and Au-Au) in the EXAFS data.³ During the fitting process, the CN values for Au-S and Au-Au were fixed at 2, as according to the structure determined by XRD results. Reported uncertainties for EXAFS fitting results were computed from off-diagonal elements of the correlation matrix, which were weighted by the square root of the reduced chi-squared value obtained from each simulated fit. The amount of experimental

noise was also taken into consideration for each Fourier transformed R-space spectrum from 15–25 Å. 4

Computational Details. DFT calculations were carried out using TURBOMOLE version 6.4^5 on the model system $[Au_8(p-SPhCO_2H)_9]^-$ built up from its corresponding X-ray structure using the hybrid PBE functional.⁶ All non metal atoms were described by using def-SV(P) basis sets.⁷ For the gold atoms we used the triple-zeta-valence quality basis sets with polarization function def2-TZVP.⁸ In the case of the gold atoms the core electrons were described using a 60-electron relativistic effective core potential.⁹ DFT/TDDFT calculations were performed on the hexanucear model $[Au_6(p-SPhCO_2H)_8]^2$ - built up from the X-ray diffraction results.

Chemicals. Tetrachloroauric acid trihydrate (HAuCl₄.3H₂O, \geq 49 % Au basis) and methanol (Chromasolv®) were purchased from Sigma-Aldrich Company and were of commercial quality and used without further purification. 4-mercaptobenzoic acid (> 95%) was purchased from TCI. The so-obtained white crystals were stored at -10 °C under air atmosphere. The glassware used in the synthesis was cleaned with aqua regia (aqua regia is a very corrosive product and should be handled with extreme care) and then rinsed with copious amount of distilled water, then dried overnight prior to use. All reactions were carried out in atmospheric conditions.

Synthesis of $[Au(p-SPhCO_2H)]_n$: HAuCl₄·3H₂O (80 mg, 0.22 mmol, 1 eq.) and 4mercaptobenzoic acid (200 mg, 1.32 mmol, 6 eq.) are dissolved in 10 ml of water in a 20 ml pillbox. During dissolving of mixture in the ultrasonic bath, the reaction turned from brown to yellow. Mixture was then heated to 120°C for 24 h. The resulting white solid was isolated by centrifuge and in a fisrt step washed with water and acetone to remove excess of *p*-HSPhCO₂H, HCl and unreacted HAuCl₄ and was dried in air. In a second step the solid is thoroughly washed with DMF to remove (*p*-SPhCO₂H)₂. Note that the inversion of the washing steps lead to the dissolution of the compound in DMF. Yield: 63 mg (89 %). All characterizations, expect structure determination, have been performed on the pure phase material synthesized at 120°C. Chemical Formula: C₇H₅AuO₂S, Molecular Weight: 350.14, Elemental Analysis (calc.) wt%: C, 24.4 (24.01); H, 1.4 (1.44); S, 9.3 (9.16). Gold content from TGA (calcd.) wt%: 56.8 (56.25).



Figure S1. PXRD patterns of $[Au(p-SPhCO_2H)]_n$ synthetized at 120 (black) and 180°C (grey). The solid has an interlamellar distance of 1.5 nm which corresponds to two tilted SPhCO₂H ligands (0.7 nm) and 0.3 nm of the gold-sulfur layer.



Figure S2. Final Rietveld plot of $[Au(p-SPhCO_2H)]_n$ showing observed (blue circles), calculated (red line), and difference (black line) curves. A zoom at high angles is shown as inset. Black asterics correspond to golf FCC present as impurity.

Empirical formula	C7 H5 S O2 Au		
Mr	350.14		
Crystal system	Triclinic		
Space group	<i>P1</i>		
<i>a</i> (Å)	4.51809(36)		
<i>b</i> (Å)	5.40840(38)		
<i>c</i> (Å)	14.86056(86)		
α (°)	84.8666(51)		
β (°)	86.2921(51)		
γ (°)	88.2557(51)		
$V(Å^3)$	360.803(44)		
Z	2		
λ (Å)	1.540598		
Number of reflections	757		
No. of fitted structural	29		
Number of soft restraints	4		
R _p , R _{wp}	0.052, 0.070		
R _{Bragg} , GoF	0.031, 5.21		
Z λ (Å) Number of reflections No. of fitted structural Number of soft restraints R _p , R _{wp} R _{Bragg} , GoF	2 1.540598 757 29 4 0.052, 0.070 0.031, 5.21		

Table S1. Crystallographic data and Rietveld refinement parameters for $[Au(p-SPhCO_2H)]_n$.

Table S2. Selected distances and angles from the structure of [Au(*p*-SPhCO₂H)]_n.

Au-Au (inter) (Å)	3.355(4), 3.422(6)
Au-Au (intra) [†] (Å)	3.591(3), 3.732(3)
Au-S (Å)	2.272(1), 2.342(5)
	2.272(8), 2.367(1)
Au-S-Au (°)	99.38(1), 110.41(4)
S-Au-S (°)	77.47(3), 124.00(1)
Au-Au-Au (inter) (°)	83.60(3)

[†] bridged by sulfur atoms.



Figure S3. Representation of the *syn, syn* catemeric hydrogen bonds in $[Au(p-SPhCO_2H)]_n$. Hydrogen donors are from O12 and O21 oxygen atoms and acceptors are O11 and O22. The distances between two oxygen atoms involved in these hydrogens interactions are 2.901(9) and 3.010(9) Å, in good accordance with the presence of hydrogen interactions.



Figure S4. SEM image of [Au(*p*-SPhCO₂H)]_n synthesized at 120°C.



Figure S5. TGA of [Au(*p*-SPhCO₂H)]_n carried out under air at 10 °C/min.



Figure S6. Zoom on the FT-IR spectra of *p*-HSPhCO₂H and $[Au(p-SPhCO_2H)]_n$. Antisymmetric vibrations of CO are present at 1677 and 1683 cm⁻¹ for *p*-HSPhCO₂H and $[Au(p-SPhCO_2H)]_n$, respectively.



Figure S7. FT-IR spectra of *p*-HSPhCO₂H and $[Au(p-SPhCO_2H)]_n$. v(OH) bands at 2560, 2670, 2830, 2980 and 3065 cm⁻¹ on the free ligand, *p*-HSPhCO₂H, and on $[Au(p-SPhCO_2H)]_n$ are proof for strong hydrogen bonds (HB) between the carboxylic acid functions.



Figure S8. ¹³C solid-state NMR of $[Au(p-SPhCO_2H)]_n$. The peaks between 139 and 128 ppm are attributed to the phenyl ring and the one at 171 ppm originates from the carboxyl group. The peaks designed by the asteric are the rotation bands.

Table S3. XPS data (quantification and position) of gold, sulfur oxygen and carbon binding energies of $[Au(p-SPhCO_2H)]_n$.

	Au	4 f	S 2	2p	O 1s	C 1s
Quantification (mol%)	8.34		6.81		14.94	69.91
Molar ratio [theoretical]	1	0.8 [1]		[1] 1.8 [2]		8.4 [7]
Peak position (eV)	Au 4f _{7/2}	Au 4f _{5/2}	S 2p _{3/2}	S 2p _{1/2}	O 1s	C 1s
	84.9	88.6	163.4	164.6	532.0 [C=O]	284.7 [C ₆ H ₄]



Figure S9. XPS analysis of $[Au(p-SPhCO_2H)]_n$ from Au 4f binding energies. The $4f_{7/2}$ and $4f_{5/2}$ binding energies of gold are at 84.9 and 88.6 eV and the position and the sharpness of the peaks with a FWHM of 1.1 eV suggest that all gold atoms are in +I oxidation state.



Figure S10. XPS analysis of $[Au(p-SPhCO_2H)]_n$ from S 2p binding energies. The S $2p_{3/2}$ and $2p_{1/2}$ binding energies occurring at 163.4 and 164.6 eV are typical of thiolate ligands and more importantly show that the sulfur atoms are not oxidized.



Figure S11. XPS analysis of $[Au(p-SPhCO_2H)]_n$ from C 1s binding energies. The main peak on the C1s binding energy at 284.7 eV is in good accordance with the phenyl groups and the contribution of the C1s from the carbonyl is located at 288.9 eV.



Figure S12. XPS analysis of $[Au(p-SPhCO_2H)]_n$ from O 1s binding energies. The O1s binding energies are located at 532.0 and 533.4 eV which correspond to the oxygen atoms from the carbonyl and hydroxyl functions, respectively. The ratio between these two peaks is around 1.

Table S4. 2D maps of the emission and excitation spectra of $[Au(p-SPhCO_2H)]_n$ carried out in solid-state at different temperatures.



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Figure S13. Excitation ($\lambda_{em} = 470 \text{ nm}$) and emission ($\lambda_{ex} = 328 \text{ nm}$) spectra of [Au(*p*-SPhCO₂H)]_n carried out in solid-state with the temperature.



Figure S14. Excitation ($\lambda_{em} = 470 \text{ nm}$) and emission ($\lambda_{ex} = 384 \text{ nm}$) spectra of [Au(*p*-SPhCO₂H)]_n carried out in solid-state with the temperature.



Figure S15. Excitation ($\lambda_{em} = 650 \text{ nm}$) and emission ($\lambda_{ex} = 340 \text{ nm}$) spectra of [Au(*p*-SPhCO₂H)]_n carried out in solid-state with the temperature.



Figure S16. Excitation ($\lambda_{em} = 534 \text{ nm}$) and emission ($\lambda_{ex} = 360 \text{ nm}$) spectra of *p*-HSPhCO₂H free ligand in solid-state at different temperatures.



Figure S17. Normalized intensities of emission ($\lambda_{ex} = 360 \text{ nm}$) spectra of *p*-HSPhCO₂H free ligand in solid-state at different temperatures.



Figure S18. 2D map of the emission and excitation spectra of p-HSPhCO₂H carried out in solid-state at 93 K.



Figure S19. Luminescence lifetime decays ($\lambda_{ex} = 379 \text{ nm}$) of $[Au(p-SPhCO_2H)]_n$ carried out in solid-state at different temperatures.



Figure S20. Plots of the light intensity for the three lifetimes τ_1 (black), τ_2 (red) and τ_3 (blue) (ns, %), obtained with a triexponantial fit of the luminescence lifetime decay from Fig. S19, as a function of the temperature for $[Au(p-SPhCO_2H)]_n$.



Figure S21. Time resolved spectroscopy for $[Au(p-SPhCO_2H)]_n$ at 93 K in solid-state. D = delay after pulse, W = width or time of acquisition (both in ns) and the pulse frequency are displayed for each curve in the legend.

Table S5. Au L₃-edge EXAFS fitting results for $[Au(p-SPhCO_2H)]_n$ and $[Au(p-SPhCO_2Me)]_n$ compounds at 300 and 90 K. R is the phase-corrected bond distance and σ^2 is the Debye-Waller factor that accounts for both structural and thermal disorder for that specific scattering path. ΔE_0 is a fitting parameter that does not provide any structural information, but can be used to help find an appropriate simulated scattering path to fit the experimental data. The coordination numbers (CN) for each path were fixed from the models constructed from XRD data.

Path	CN	R (Å) (300 K / 90 K)	σ ² (Å ²) (300 K / 90 K)	ΔE_0 (eV)			
[Au(p-SPhCO ₂ H)] _n							
Au-S	2	2.316(4) / 2.320(5)	0.0022(2) / 0.0014(2)	0(1) / 2(1)			
Au-Au (inter)	2	3.4(1) / 3.42(2)	0.02(1) / 0.006(1)	0(1) / 2(1)			
Au-Au (intra)	2	4.06(3) / 3.97(3)	0.008(1) / 0.007(3)	0(1) / 2(1)			
[Au(p-SPhCO ₂ Me)] _n							
Au-S	2	2.321(5) / 2.301(3)	0.0024(2) / 0.0017(1)	0(1) / -2.3(7)			
Au-Au (inter)	2	3.19(8) / 3.16(1)	0.014(6) / 0.0018(5)	4 / 9			
S-Au-S (MS)	2	4.63(6) / 4.71(2)	0.006(2) / 0.003(1)	2 / 7			



Figure S22. Au L₃-edge FT-EXAFS spectra of $[Au(p-SPhCO_2H)]_n$ and $[Au(p-SPhCO_2Me)]_n$ compounds at 300 and 90 K.

Au L₃-edge FT-EXAFS spectra at 300 and 90 K for both thiolate ligand types show a dominant Au-S scattering peak centred at 2 Å (non-phase corrected). Following this, from ~2.5 to 4.5 Å, a combination of Au-C, Au-S, and Au-Au scattering paths contribute to the scattering features. More prominent in this region are the Au-Au scattering peaks since the backscattering Au atom is heavier. The data for $[Au(p-SPhCO_2H)]_n$ can be fitted with one Au-S and two Au-Au scattering paths. The bond distances for Au-S and intermolecular Au-Au paths are consistent with the bonding data from XRD results. There are two Au-Au scattering paths that account for two types of Au-Au bonding, inter- and intramolecular interactions (Table S5). Intramolecular Au-Au interactions are longer than what was shown from XRD data. This system does not show a significant thermal contraction property and the Au-Au scattering peak is less intense than seen for $[Au(p-SPhCO_2Me)]_n$, especially at 90 K. This confirms the effect of hydrogen bonding inducing the rigidity of the coordination polymer network and offers an explanation for the less emissive properties of $[Au(p-SPhCO_2H)]_n$.



Figure S23. Overlapped Au L₃-edge FT-EXAFS spectra of $[Au(p-SPhCO_2H)]_n$ and $[Au(p-SPhCO_2Me)]_n$ compounds at 300 and 90 K.





Figure S24. Electronic structure with frontier molecular orbitals (MOs) computed at DFT level of theory for the model systeme $[Au_8(p-SPhCO_2H)_9]^-$.

Excitation	λ_{exc} (nm)	Osc. strength ^a	Contributions ^b	
2	466.9	0.656 x 10 ⁻²	$H \rightarrow L+1 (94.8)$ LM to M CT	
3	457.9	0.122	$H \rightarrow L (75.5) L \text{ to } M \text{ CT}$ $H-2 \rightarrow L (11.6) L \text{ to } M \text{ CT}$	
4	447.3	0.33 x 10 ⁻²	H-1 → L+1 (48.6) L to M CT H-2 → L (28.6) L to M CT H-3 → L (18.8) L to M CT	
5	442.0	0.18 x 10 ⁻¹	H-1 \rightarrow L+1 (40.8) L to M CT H-2 \rightarrow L (40.1) L to M CT	
7	432.8	0292 x 10 ⁻¹	H-3 \rightarrow L (45.1) L to M CT H \rightarrow L+2 (25.8) L to M CT	
8	419.6	0.506 x 10 ⁻²	H-4 \rightarrow L (45.8) L to M CT H-2 \rightarrow L+1 (28.7) L to M CT H-1 \rightarrow L+2 (18.3) L to M CT	
9	413.3	0.026 x 10 ⁻²	H-4 → L (32.3) L to M CT H-1 → L+2 (30.6) L to M CT H-3 → L+1 (20.2) L to M CT	

Table S6. TD-DFT of the first 70 computed singlet-singlet excitations with the oscillator strength and the attribution of the main contributions.

13	385.7	0.895 x 10 ⁻²	H-2 → L+2 (58.6) L to M CT H-3 → L+1 (10.6) L to M CT
14	374.4	0.261 x 10 ⁻²	H-1 → L+3 (42.2) L to M CT H-3 → L+2 (36.0) L to M CT
15	373.3	0.552 x 10 ⁻²	H-1 → L+3 (57.1) L to M CT H-3 → L+2 (23.7) L to M CT
16	368.1	0.219 x 10 ⁻²	$H \rightarrow L+3 (54.7) L$ to M CT H-5 $\rightarrow L (40.0) L$ to M CT
18	362.2	0.263 x 10 ⁻²	$H-5 \rightarrow L (56.0) L \text{ to } M \text{ CT}$ $H \rightarrow L+3 (32.2) L \text{ to } M \text{ CT}$
20	352.4	0.113 x 10 ⁻²	$H-2 \rightarrow L+3$ (86.6) L to M CT
32	330.6	0.123 x 10 ⁻²	H-13 → L (30.5) L to M CT H-10 → L (24.2) L to M CT H-12 → L (22.1) L to M CT
39	322.6	0.125 x 10 ⁻²	$H-6 \rightarrow L+2 (64.9) L$ to M CT $H-8 \rightarrow L+1 (23.3) L$ to M CT
40	320.9	0.210 x 10 ⁻²	H-14 \rightarrow L (66.1) L to M CT H-15 \rightarrow L (13.0) L to M CT
50	310.1	0.901 x 10 ⁻²	H-1 \rightarrow L+6 (81.8) L to L CT
69	295.4	0.585 x 10-2	$H \rightarrow L+9$ (71.2) IL and L to L CT
70	295.0	0.571 x 10-2	$H-2 \rightarrow L+5 (72.9) \text{ IL}$

^a The oscillator strength (f) shows the mixed representation of both velocity and length. ^b The value is 2 x $|coeff|^2$ x100.



Figure S25. TD-DFT of the first 70 computed singlet-singlet excitations.



Figure S26. Simplistic energy diagram of the dual emission of [Au(p-SPhCO₂H)]_n.



Figure S27. Emission spectra ($\lambda_{ex} = 328 \text{ nm}$) normalized with 650 nm peak intensities of [Au(*p*-SPhCO₂H)]_n carried out in solid-state with the temperature.



Figure S28. Plots of the emission intensities ($\lambda_{ex} = 328 \text{ nm}$) of peaks centered at 490 nm (I_{HE}) and 650 nm (I_{LE}). The intensities, I_{HE} and I_{LE} , are determined by the integration of the emission spectra between 455 and 550 nm and 625 and 650 nm, respectively.



Figure S29. Plot of the I_{HE}/I_{LE} ratio with the temperature. The red line corresponds to the polynomial fit between 80 and 320 K.

To show how important change of parameters used for temperature sensing is both absolute and relative sensitivity are used. However, in order to have possibility to objectively compare the performances of the different luminescent thermometers, likewise thermometers that operate by different mechanisms or that are based on different material systems, the relative sensitivity (S_r) is usually utilized and is defined as:

$$S_r = \frac{\partial P / \partial T}{P}$$

where P is the measured temperature-sensitive parameter, such as intensity, lifetime, wavelength or intensity ratio, and T is temperature.

The relative sensitivity varies with the temperature and reaches its maximal value of 2.96 %.K⁻¹ at 260 K. The evolution of the relative sensitivity does not change monotonously, but possesses two local minima at 190 and 300 K corresponding to the temperature ranges where the slope becomes steeper (Fig. S26).



Figure S30. The I_{HE}/I_{LE} ratio (red line) and the temperature-dependent relative sensitivity (*S_r*) (black circles) of $[Au(p-SPhCO_2H)]_n$.

Table S7. Comparison of sensitivities of other reported ratiometric luminescent MOF-based thermometers with $[Au(p-SPhCO_2H)]_n$, including the origine of the dual emission, the working temperature range (K), the maximum relative sensitivity value (S_r , % K⁻¹) and the temperature at which S_r is maximum (T_r , K).¹⁰

Luminescent MOF	Origine [§]	Temperature [K]	<i>S</i> _r [% K ^{−1}]	<i>T</i> _r [K]
[Au(p-SPhCO ₂ H)] _n	Intrinsic	80-320	2.96	260
ZnATZ-BTB	Intrinsic	30-130	5.29	30
Dycpia	Intrinsic	298-473	0.42	473
Eu _{0.0069} Tb _{0.9931} -DMBDC	La dopping	50-200	1.15	200
Tb _{0.9} Eu _{0.1} PIA	La dopping	100-300	3.27	300
Tb _{0.50} Eu _{0.50} PIA	La dopping	75–275	2.02	275
Tb _{0.98} Eu _{0.02} -OA-DSTP	La dopping	77–275	2.40	275
Tb _{0.98} Eu _{0.02} -BDC-DSTP	La dopping	77–225	2.75	225
Tb _{0.957} Eu _{0.043} -cpda	La dopping	40-300	16.0	300
Eu _{0.7} Tb _{0.3} -cam-Himdc	La dopping	100-450	0.11	450
Eu _{0.02} Gd _{0.98} -DSB	La dopping	20-300	4.75	20
$Tb_{0.99}Eu_{0.01}(BDC)_{1.5}(H_2O)_2$	La dopping	290-320	0.31	318
Eu _{0.0616} Tb _{0.9382} pcdmb	La dopping	25-200	0.34	200
Eu _{0.5} Tb _{99.5} @In(OH)bpydc	La dopping	283-333	2.53	333
ZJU-88⊃perylene	Orga dopping	293–353	1.28	293
TbTATAB⊃C460	Orga dopping	100-300	4.48	300

[§]La dopping : Lanthanide dopping ; Orga dopping: organic molecule dopping.



Figure S31. Visual comparison of the maximum relative sensitivity values (S_r , % K⁻¹) with the working temperature ranges (K) of the reported ratiometric luminescent MOF-based thermometers with $[Au(p-SPhCO_2H)]_n$.¹⁰



Figure S32. Emission spectra ($\lambda_{ex} = 328 \text{ nm}$) of $[Au(p-SPhCO_2H)]_n$ carried out at 290 K and 100 K over three cycles.

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