Nonradiative deactivation of Europium (III) luminescence as a detection scheme for moisture

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General information

Unless otherwise noted, all reactions were carried out under argon in pre-dried glassware using Schlenk techniques. Materials were obtained from commercial sources (Aldrich, Fluka or Lancaster) and were used without further purification.

CH₂Cl₂ was dried by distillation over CaH₂ and degassed with argon. NMR spectroscopy was performed on a VARIAN INOVA 500 MHz spectrometer. The frequencies for ¹H were 499.83 MHz and 125.69 MHz for ¹³C, respectively. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. For europium-containing samples, the relaxation delay was set to 2s in order to guarantee complete relaxation. Chemical shifts are given in ppm relative to a SiMe₄ standard. Solvent residual peaks were used for referencing the NMR-spectra to the corresponding values given in literature [1]. Peak shapes are indicated as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), b (broad), v (virtual splitting).

Gel permeation chromatography (GPC) was used to determine molecular weights and the polydispersity index (PDI). Measurements were carried out in THF with the following arrangement: a Merck Hitachi L6000 pump, separation columns of Polymer Standards Service (5 μ m grade size) and a refractive-index detector from Wyatt Technology. For calibration, polystyrene standards purchased from Polymer Standard Service were used.

MALDI-TOF mass spectrometry was performed on a Micromass TofSpec 2E Time-of-Flight Mass Spectrometer. The instrument is equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz) and a time lag focusing unit. Ions were generated by irradiation just above the threshold laser power. Positive ion spectra were recorded in reflectron mode applying an accelerating voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethyleneglycol)s (PEG). The spectra of 100-150 shots were averaged. Analysis of data was done with MassLynx-Software V3.5 (Micromass/Waters, Manchester, UK). Samples were dissolved in THF (c=1 mg/ml), dithranol was used as matrix (c=10 mg/ml in THF). Solutions were mixed in the cap of a microtube in the ratio of 1 μ I:10 μ I. 0.5 μ I of the resulting mixture were spotted onto the target and allowed to air dry. X-ray diffraction data were collected by using a Bruker Smart [2] APEX CCD system, graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å), and $0.3^{\circ}\omega$ -scan frames covering a complete sphere of the reciprocal space with $\theta_{max} = 28.34^{\circ}$. After data integration and unit cell refinement with program SAINT, [2] a multi-scan absorption correction with program SADABS [2] was applied to the data. The structure was solved with direct methods and was expanded to completeness by successive Fourier syntheses using program SHELXS97.[3] Structure refinement on F^2 was carried out with the program SHELXL97 [3] using anisotropic temperature factors for all non-hydrogen atoms and U_{ij} constraints for one of the six pentane solvent molecules. Partial orientation disorder of the twelve independent 2-thienyl groups was taken into account. Hydrogen atoms were inserted in calculated positions and subsequently treated as riding.

Preparation of ligands



Figure S1: Nitrogen donor ligands 6, 6a and 7

2-Phenyl-1H-imidazo(4,5-f)(1,10)-phenanthroline (6a) was prepared as previously described by Shavaleev et al.[4] The bidentate ligand 6 and the tridentate ligand 7 were both prepared using 4-hexyloxybenzaldehyde as starting material.



Figure S2: Ligand synthesis starting with 4-hexyloxybenzaldehyde



Preparation of 2-(4-Hexyloxyphenyl)-1H-imidazo(4,5-f)(1,10)phenanthroline (6)

Figure S3: Preparation of 6

The preparation of **6** was carried out as described in a recent paper from our group [5]. 200 mg of 5,6phenanthrolindione (0.95 mmol, 1 equiv.), 294 mg of p-hexyloxybenzaldehyde (1.5 equiv., 1.42 mmol) and 1.5 g ammonium acetate (19 mmol, 20 equiv.) were placed in a 100 mL Schlenk tube. 4 mL of glacial acetic acid were added and the reaction mixture was heated up to 120 °C for 12 h.

The reaction mixture showed a dark brown color and product formation was detected by TLC (chloroform/methanol 9/1 or dichloromethane/acetone 5/1). The reaction was worked up by addition of 20 mL of distilled H_2O , followed by precipitation of a dark brown solid. Because this solid was too sticky for filtration, the aqueous solution was extracted with 50 mL of dichloromethane three times. After drying and solvent evaporation, the resulting red oil was recrystallised from acetone/dichloromethane to yield a yellow solid. Yield: 294 mg (56%).

Anal. calc'd. for $C_{25}H_{24}N_4O$ (396.49 g/mol): C, 75.73; H, 6.10; N, 14.13; found: C,75.60; H, 6.11; N, 14.15;

¹H-NMR (δ, 20 °C, 500 Hz, dmso-d⁶): 8.93 – 8.97 (m, 4H, phen^{2,4,7,9}), 8.25 (d, 2H, J=8.4 Hz, ph^{2,6}), 7.79 (m, 2H, phen^{3,8}), 7.12 (d, 2H, J=8.4 Hz, ph^{3,5}), 4.06 (t, 2H, J=5.7 Hz, CH_2O hex¹), 1.74 (m, 2H, J=7.1 Hz, CH_2 hex²), 1.45 (m, 2H, CH_2 hex³), 1.36-1.30 (m, 4H, CH_2 hex^{4,5}), 0.89 (t, 3H, CH_3 hex⁶)

¹³C{¹H}-NMR ($\bar{0}$, 20 °C, 125 MHz, dmso-d⁶): 160.3 (1C, ph⁴), 152.4, 148.0, 143.9, (3C, phen^{2,9}, N-*C*=N), 130.4, 128.5, 124.0, 123.8 (12C, ph^{2,6}, phen^{3,4,4a,4b,5,6,6a,7,8,10.10a,10b}), 115.4 (2C, ph^{3,5}), 68.3 (1C, *C*H₂-O), 31.7, 29.3, 25.9, 22.8 (4C, *C*H₂^{2,3,4,5}), 14.6 (1C, *C*H₃)



Figure S4. 1H-NMR (500 MHz, CDCl₃) of 6

Preparation of 4'-(4-Hexyloxyphenyl)-(2,2':6',2")terpyridine (7)



Figure S5: Preparation of 6

200 mg of sodium hydroxide (5 mmol, 2.66 equiv.) were suspended in 6 mL of PEG 300 and 456 mg (422 μ L, 3.76 mmol, 2 equiv.) of 2-acetylpyridine were added dropwise. The solution turned red and after 1 h of stirring at room temperature, 388 mg of hexyloxybenzaldehyde (1.88 mmol, 1 equiv.) were added. The reaction vessel was stirred for further 2.5 h at ambient temperature, then for 1 h at 50 °C. After TLC proved that no more acetylpyridine was present in the reaction mixture, 1.5 mL of conc. NH₃ were added causing a color change to brown. The vessel was then heated up to 100 °C and after 1 h, the reaction mixture was transferred to a separatory funnel with 50 mL of dichloromethane and extracted with 50 mL of distilled H₂O (due to the polyethylene glycol, layer separation takes several hours). After drying and evaporation, 3.3 g of a brownish oil were obtained which were purified by column chromatography (cyclohexane/ethyl acetate 10:1).Yield: 340 mg (44%) of a white, crystalline solid.

Anal. calc'd. for $C_{27}H_{27}N_3O$ (409.53 g/mol): C, 79.19; H, 6.65; N, 10.26; found: C, 79.15; H, 6.59; N, 10.29.

¹H-NMR (δ , 20 °C, CDCl₃, 500 MHz): 8.74 (m, 2H, py^{6,6"}), 8.71 (s, 2H, py^{3',5"}) 8.67 (m, 2H, py^{3,3"}), 7.89 (m, 4H, py^{4,4"}, ph^{3,5}), 7.36 (ddd, 2H, J=1 Hz, J=2.6 Hz, J=4.8 Hz, ph^{2,6}), 7.03 (dt, J=2.8 Hz, J=8.7 Hz, py^{5,5"})) 4.03 (t, 2H, J=6.6 Hz, CH₂-O hex¹), 1.84 (m, 2H, CH₂ hex²), 1.50 (m, 2H, CH₂ hex³), 1.37 (m, 4H, CH₂ hex^{4,5}), 0.92 (t, 3H, J=6.9 Hz, CH₃hex⁶ CH₃)



Preparation of phosphorescent dyes

Preparation of tris(1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato-O,O')europium(iii) dihydrate (1)

Eu $(TTA)_3(H_2O)_2$ was prepared after a modified literature procedure [6]. 992.6 mg of 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione (4.47 mmol, 3 equiv.) were dissolved in 20 mL of ethanol and the pH of this solution was set to 11 with sodium hydroxide. To the resulting yellowish solution, an aqueous solution (8 mL) of EuCl₃·6H₂O (550.6 mg, 1.5 mmol, MW: 366.41, 1eq) was added dropwise.

Afterwards, 50 mL of H_2O were added (which caused formation of a white precipitate) and the resulting suspension was stirred for 45 min at 60 °C. After cooling to ambient temperature, the precipitate was collected by filtration, washed with water and dried *in vacuo*. Yield: 916mg (71.6%) of a yellowish solid (red emission is observed under UV light of a wavelength of 365 nm).

Anal. calc'd. for C₂₄H₁₆O₈S₃F₉Eu: C, 49.38; H, 2.76; N, 0.00; found: C, 49.44; H, 2.81; N, 0.01.

¹H-NMR (δ, 20 °C, acetone-d⁶,500 MHz): 7.07 (d, 3H, J = 8.7 Hz, J = 4.7), 6.14 (s, 3H), 5.5 (s, 7.5H), 5.2 (s, 3H)



Figure S7. 1H-NMR (500 MHz, CDCl₃) of 1

Preparation of Eu(6)(TTA)₃ (2-(4-Hexyloxyphenyl)-1H-imidazo(4,5-f)(1,10)phenanthroline-N,N')-tris(1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato-O,O')-europium(iii) (2)





A mixture of **6** (50 mg, 0.127 mmol, 1 equiv.) and EuCl₃·6H₂O (42.6 mg, 0.127 mmol, 1 equiv.) were stirred in 5 mL of absolute ethanol under argon for 2 h at 80 °C. Initially, a gel formed but no red emission was observed when the reaction mixture was viewed under 365 nm UV light. Then, a mixture of TTA (84.5 mg, 0.380 mmol, 3 equiv.) and KO^tBu (42.6 mg, 0.380 mmol, 3 equiv.) in 2 mL of absolute ethanol was added. This caused to liquify the gel again and to form a yellow precipitate instead. The reaction mixture was stirred for 2 h under argon at 80 °C, then at room temperature overnight. 10 mL of deonized water were added to the reaction mixture and a yellowish, red-emitting precipitate was formed. The vessel was stirred at room temperature for 1 h and put into the freezer for 4h. The solid was collected, washed with 10 mL of H₂O dest. and 3 mL of n-pentane and dried *in vacuo*.

Yield: 120 mg (64%). The yellow, powdery solid exhibits bright red emission when excited at 365 nm.

¹H-NMR (δ, 20 °C, 500 MHz, CDCl₃): could not be interpreted due to broadening of peaks

MALDI-TOF MS: found 989.101 (calc'd. 989.092) for [6Eu(TTA)2+]

Anal calc'd. for $C_{49}H_{36}N_4O_7S_3F_9Eu$ (1211.4 g/mol) : C, 48.58; H, 3.00; N, 4.62; found: C,48.81; H, 3.05; N, 4.60.

In order to further clarify the structure of $Eu(6)(TTA)_3 2$, a series of several europium complexes with differently substituted nitrogen donor ligands and TTA as coligand was synthesised. It was attempted to obtain suitable crystals for X-Ray diffractometry by n-pentane diffusion, which was successful for the unsubstituted imidazophenanthroline ligand **6a**.

Preparation of $Eu(6a)(TTA)_3$ (2-Phenyl-1H-imidazo(4,5-f)(1,10)phenanthroline-N,N')-tris(1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato-O,O')-europium(iii) (2a)



Figure S9 Preparation of 2a

A mixture of **6a** (50 mg, 0.169 mmol, 1 equiv.) and EuCl₃·6H₂O (56.8 mg, 0.169 mmol, 1 equiv.) was stirred in 5 mL of absolute ethanol under argon for 2 h at 80 °C. Initially, a gel was formed and no red emission was observed when the reaction mixture was viewed under 365 nm UV light. Then, a mixture of TTA (112.6 mg, 0.507 mmol, 3 equiv.) and KO^tBu (56.9 mg, 0.507 mmol, 3 equiv.) in 2 mL of absolute ethanol was added. This caused to liquify the gel again and to form a yellow precipitate instead. The reaction mixture was stirred for 2 h under argon at 80 °C, then at room temperature overnight. 10 mL of H₂O dest. were added to the reaction mixture and a yellowish, red-emitting precipitate was formed. The vessel was stirred at room temperature for 1 h and put into the freezer overnight. The solid was collected, washed with 10 mL of H₂O dest. and 3 mL of n-pentane and dried *in vacuo*. 123 mg (64%) of a yellow powder were obtained. The compound exhibits bright red emission when excited at 365 nm.

¹H-NMR (δ, 20 °C, 500 MHz, CDCl₃): could not be interpreted due to broadening of peaks

MALDI-TOF MS: found 888.998 (calc'd. 889.003) for [6aEu(TTA)2⁺]

Anal calc'd. for $C_{43}H_{24}N_4O_6S_3F_9Eu$ (1111.2 g/mol) : C 46,48; H, 2.18; N, 5.04, found: C 46,97; H, 2.21; N, 5.08.

Preparation of (4'-(4-Hexyloxyphenyl)-(2,2':6',2'') terpyridine)N,N',N'')-tris(1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato-O,O')-europium(iii) Eu $(7)(TTA)_3$ (3)





A mixture of **7** (50 mg, 0.122 mmol, 1 equiv.) and EuCl₃·6H₂O (41.1 mg, 0.122 mmol, 1 equiv.) were stirred in 5 mL of absolute ethanol under argon for 2 h at 80 °C. The reagents did not dissolve entirely and red emission was observed upon excitation at 365 nm. Then, a mixture of TTA (81.3 mg, 0.366 mmol, 3 equiv.) and KO^tBu (41.1 mg, 0.366 mmol, 3 equiv.), was added. A white solid was formed and the reaction mixture was stirred for 2 h under argon at 80 °C, then at room temperature overnight. 10 mL of H₂O dest. were added to the reaction mixture and a white, red-emitting precipitate was formed. The vessel was put into the freezer overnight. The solid was collected, washed with 10 mL of H₂O dest. and 3 mL of n-pentane and dried *in vacuo.* 90 mg (60%) of a yellowish solid were obtained.

¹H-NMR (δ, 20 °C, 500 MHz, CDCl₃): 12.99 (b, 2H, *L2*), 10.80 (b, 2H, *L2*), 8.40 (b, 2H, *L2*), 7.35 (d, 2H, J=7.75, *L2*), 7.03-6.90 (m, 7H, 4H(*L2*, ph)+3H (*TTA*)), 6.23 (b, 3H, *TTA*), 5.56 (b, 3H, *TTA*), 4.03 (m, 2H, hex¹), 1.81 (b, 2H, hex²), 1.46 (b, 2H, hex³), 1.35 (b, 4H, hex^{4.5}), 0.91 (b, 3H, hex⁶)

MALDI-TOF MS: found 1002.119 (calc'd. 1002.112) for [7Eu(TTA)₂⁺]

Anal calc'd. for $C_{51}H_{39}N_3O_7S_3F_9Eu$ (1224.4 g/mol) : C, 50.03; H, 3.21; N, 3.43; found: C, 50.25; H, 3.22; N, 3.49.



UV-VIS absorption and photoluminescence studies

UV-VIS absorption and photoluminescence spectra of all β -diketonate-based dyes were recorded from diluted THF solutions of the respective compounds. The molar extinction coefficients were determined by the Beer-Lambert equation.

The results for 2, 2a and 3 are summarised in Table S1.

Table S1 UV-VIS absorption and photoluminescence spectra of TTA-based dyes

absorption	PL in solution				
	excitation	emission			
λ _{abs} [nm]	λ _{ex} [nm], λ _{exc} =614 nm	λ _{em} [nm], λ _{ex} =350 nm			
$(\epsilon [10^{3} L mol^{-1} cm^{-1}])$	(relative excitation intensity)	(relative emission intensity)			
282 (36.0), 341	343 (1)	422 (0.036)*, 580 (0.031), 596 (0.068), 615 (1) ,			
(52.5)	364** (0.78)	653 (0.037)			
279 (76.3), 299**	342 (1)	410* (0.032), 580 (0.027), 596 (0.065), 615 (1) ,			
(58.1),	361** (0.80)	654 (0.034)			
339 (67.8)					
287 (57.1), 343	355	412 (0.036)* 580 (0.030), 588** (0.043), 597			
(59.8)		(0.071), 616 (1) , 653 (0.037)			
	absorption λ _{abs} [nm] (ε [10 ³ L mol ⁻¹ cm ⁻¹]) 282 (36.0), 341 (52.5) 279 (76.3), 299** (58.1), 339 (67.8) 287 (57.1), 343 (59.8)	absorption PL in solution Λ_{abs} [nm] λ_{ex} [nm], λ_{exc} =614 nm (ϵ [10 ³ L mol ⁻¹ cm ⁻¹]) (relative excitation intensity) 282 (36.0), 341 343 (1) (52.5) 364** (0.78) 279 (76.3), 299** 342 (1) (58.1), 361** (0.80) 339 (67.8) 287 (57.1), 343 287 (57.1), 343 355			

* broad, ligand-centred emission

**shoulder

All of these spectra have in common that two absorption maxima are present, one lying in the range of 270 to 300 nm, the other located between 340 and 350 nm. The 4-(O-hexyl)phenyl-substituted complex **6**, shows a small bathochromic shift of both excitation maxima compared to the phenyl-substituted complex **6**.

The emission spectra show the typical line spectrum observed in europium complexes with the most intensive peak around 615 nm. The intensity of the other europium lines varies, depending on the ligand, but in general, similar spectra are obtained. In some of the complexes, residual ligand emission was observed, suggesting that either the products are contaminated with excess ligand or the energy transfer is not fully efficient.

Matrix homopolymers

Table S2 gives an overview of the commercially available polymers which were used to benchmark the polynorbornene in terms of performance.



Table S2 Commercially available matrix polymers

General Procedure for synthesis of poly(norbornenes)

Monomers and Initiators

 $RuCl_2(pyridine)_2(H_2IMes)(CHPh)$ [7] (H2IMes= N,N-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) and (±)exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester **4** were prepared according to literature [8]. (±)-*exo,endo*-5,6-bis(methoxymethyl)bicyclo[2.2.1]hept-2-ene (**5**) was obtained from the corresponding alcohol after a previously published procedure.[9]

Polymerisation

ROMP polymers were prepared according to a general procedure: 300 equiv. or 100 equiv. of the respective monomer (about 500 mg) were dissolved in 5 mL of dry, degassed CH_2Cl_2 . Subsequently, 1 equiv. of $RuCl_2(pyridine)_2(H_2IMes)(CHPh)$ was added at once (dissolved in 1 mL of dry, degassed CH_2Cl_2). The initially green solution turned yellow upon initiation and was stirred for about 1 h (reaction progress was monitored by TLC using cyclohexane/ethyl acetate 5/1 and KMnO₄ for staining). After complete monomer consumption had been detected, the reaction was quenched by adding 150 μ L of ethyl vinyl ether and stirred for further 15 min. Then, the solution was concentrated to a volume of about 1 mL and the polymers were precipitated by dropwise addition of this solution to 200 mL of cold stirred methanol, collected and dried *in vacuo*.

Table S3 Matrix poly(norbornenes)							
Monomer	Yield [%]	M _n [g/mol]	PDI	¹ H-NMR (δ, 20 ℃, 500 MHz, CDCl ₃)			
poly-4 1:100 $\int_{100}^{100} \int_{100}^{100} \int$	58	21340	1.05	5.60-5.15 (m, 2H, C <i>H</i> =C <i>H</i>), 3.74-3.61 (m, 6H, COO-C <i>H</i> ₃), 3.30-2.73, 2.09-1.86, 1.54-1.46 (bs, 6H, cp ^{1,2,3,4,5})			
poly-5 1:300 $f_{1}^{(1)} = f_{1}^{(1)} = f$	76	66780	1.04	5.45-5.20 (m, 2H, C <i>H</i> =C <i>H</i>), 3.45-3.20 (m, 10H, C <i>H</i> ₂ -O, C <i>H</i> ₃ -O), 3.05-2.80, 2.70-2.50, 2.30-2.05, 1.90-1.60, 1.40-1.20 (bs, 6H, cp ^{1,2,3,4,5})			

Measuring setup

The optical measurements were carried out in a custom-made stainless steel flow-through setup (V=25 mL). All optical components were directly integrated into the cover of the measurement chamber. To avoid ingress of oxygen or other interfering quenchers, a circular purge flow was also integrated (Figure S12).



Figure S12 Photograph (top view) of the measuring cavity and schematic draw of the measuring setup The phase-sensitive signal was monitored via a setup consisting of an optoelectronic readout module directly integrated into the cover of the measuring cavity. Thereby, the intensity of the excitation light source is modulated with a suitable frequency **f** (228 Hz). Due to the luminescence lifetime of the probe, which changes with different moisture content, the response is delayed. This results in a phase shift Φ (which is a function of the luminescence lifetime τ as described in Equation S1) between reference excitation and emission light, which is measured. [10] A set of optical filters (SCHOTT BG12, thickness 2 mm for the excitation source and SCHOTT OG550 for the photodiode) was also included in the measurement setup to separate the luminescence signal from the excitation light and other optical background signals.



Figure S13: Principle of frequency domain time-resolved measurements

Sensor spots

For preparation of sensor spots, solutions of the respective dyes and matrix polymers in THF were mixed so that a final concentration of 10 mg/ml polymer and 5 wt% dye (with respect to the polymer) was obtained. 100 μ l of the resulting solution were spotted onto a glass slide to obtain sensor spots with a diameter of around 1.5 cm.

Reference system

For referencing, the measuring cavity is equipped with a capacitive humidity sensor (EE35, E+E Elektronik, Austria) which served as reference.

Humidity generator

For the generation of defined amounts of moisture, a setup similar to the one described by McGaughey et al. was developed which consisted of a two-temperature humidity generator and a gas mixer unit.[11] This allowed to obtain a reference system with an good reliability in combination with acceptable response times.

In a two-temperature humidity generator, a dry gas stream is bubbled through water bottles which are kept at a temperature significantly lower than the rest of the system (to avoid condensation). The temperature in the saturator bottles is defining the final amount of moisture in the resulting gas stream which is determined by the dew point (the point where the actual water vapour pressure equals the saturation water vapour pressure).

The dew point can be expressed as a function of saturation vapour pressure assuming full saturation according to Equation S2 (at a normal pressure of 1013.25 hPa). [12]

$$T_{d} = 241.2 \cdot \left[17.5043 \cdot \left(\ln \frac{e_{w}}{6.11213} \right)^{-1} - 1 \right]^{-1} \qquad \begin{array}{c} \mathsf{Td} \ [\,^{\circ}\mathsf{C}\,] & \text{dew point} \\ \mathsf{e}_{w} \ [\mathsf{hPa}] \text{actual saturation water} \\ \text{vapour pressure} \\ \text{(above water)} \end{array} \right]$$
(Eq. S2)

At temperatures below -30 °C, the frost point has to be used and can be calculated in analogy to the dew point, according to Equation S3 at normal pressure.

$$T_{f} = 272.186 \cdot \left[22.4433 \cdot \left(\ln \frac{e_{i}'}{6.11153} \right)^{-1} - 1 \right]^{-1} \qquad \begin{array}{c} \mathsf{T}_{f} & \text{frost point} \\ \mathsf{e}_{i}' \text{ [hPa] actual saturation} \\ \text{water vapour} \\ \text{pressure (above ice)} \end{array} \right]$$
(Eq. S3)

From these values, the absolute moisture content can be derived according to Equation S4 as the ratio of the volume of vapour V_v to the total volume of the humid air V at a given pressure p (for the sake of simplicity, a normal pressure of 1013.25 hPa was assumed).

$$w_{v} = \frac{V_{v}}{V} = \frac{e'}{p}$$

$$w_{v} [ppm] volume ratio$$

$$V_{v} [m^{3}] volume of water vapour$$

$$V [m^{3}] total volume$$

$$e'[hPa] water vapour pressure$$

$$p[hPa] total pressure$$
(Eq. S4)

For the saturation device as shown in the paper, four cavities were drilled into an aluminium block. Two of these cavities are used as saturators (bubblers equipped with porous metal endings) and the other two are left empty. The cavities are covered with an aluminium plate that is equipped with stainless steel tubing (together with Teflon seals) to connect the cavities with each other. All four cavities are surrounded by Viton O-rings to seal the nitrogen gas stream from ambient interferent such as CO_2 and O_2 . For thermostabilising, four Peltier Elements (PE-071-14-25-S from SuperCool) were used.

Mass-flow controllers (get red-y SMART GSC-AT9A-BB21, vögtlin) were used for mixing the moisturised gas stream with the "zero gas" (nitrogen 5.0 as obtained from Linde). The optoelectronic readout device, the reference humidity sensor and the mass flow controllers are connected to a PC via different interfaces and can be addressed directly by a LabView based software allowing automatized measurements. Table S2 and Figure S14 shall give an idea about the performance of the calibration system. Herein, the theoretically calculated values according to Equation(s) S2 – S4 for generated moisture amounts are compared to the values measured by the capacitive reference humidity sensor described above. Four subsequent measurements resulting in a curve as presented in Figure S14 were evaluated in order to obtain values for the dew points at different moisture levels.

measured dew point temperatures doing Eq. 32-34/							
Saturator temperature [°C]	Dew point _{th} [℃]	e' _{th} [hPa]	Dew point _{act} [℃]	e' _{act} [hPa]	Saturation [%]		
20	20	23.49	16.8±0.34	19.2	81.8		
15	15	17.12	12.5±0.04	14.5	84.9		
10	10	12.33	7.4±0.16	10.3	83.6		
4.5 (minimum)	4.5	8.46	2.7±0.31	7.5	88.1		

Table S3. Theoretically obtained dew point values (saturation vapour pressure at the respective saturator temperature) compared to the actually observed values (hPa values were calculated from measured dew point temperatures using Eq. S2-S4)

These values for 100% of humid air were then used to calculate theoretical dew point values for the different dilution levels. These theoretical values were then compared with the results from our measurements and the latter were used to calculate the absolute moisture amount in ppm_v (Table S4). Figure S15 shows an according plot.

Table S4 Comparison of the theoretically calculated vs. the measured dew points after the dilution stage

T _{set} (saturator) [℃]	Dew point act [°C]	e' _{act} [hPa]	Mixing ratio [% moist N ₂]	e' _{th} [hPa]	Dew point _{th} [℃]	Dew point _{act} [℃]	abs. humidity [ppm _v]
20	16.85	19.21	100	19.21	16.89	16.85	19023
			50	9.61	6.40	6.16	9369
			5	0.96	-20.73	-20.71	956
			1	0.19	-36.35	-35.16	218
15	12.51	14.54	100	14.54	12.56	12.51	14373
			50	7.27	2.41	2.15	7070
			5	0.73	-23.58	-23.66	716
			1	0.15	-38.87	-37.78	163
10	7.47	10.31	100	10.31	7.43	7.47	10252
			50	5.16	-2.05	-2.24	5028
			5	0.52	-27.01	-26.80	523
			1	0.10	-41.89	-40.25	124
4.5	2.92	7.45	100	7.45	2.76	2.92	7468
			50	3.72	-5.88	-6.16	3604
			5	0.37	-30.17	-29.70	389
			1	0.07	-44.68	-41.60	106

A linear relationship between the theoretical and observed dew points together with the only small deviations from this line shows that the humidity concentrations generated in the measuring setup are well reproducible.



theoretically calculated dew/frost point [°C]

Figure S15 Comparison of theoretically calculated and observed dew points as created in the moisture generator

In order to avoid condensation in the tubings or in the measuring device itself, the temperature at which the saturator was run was chosen to be $4.5 \,^{\circ}$ C (the minimum temperature which was possible with the setup at hand).

Therefore, the following settings were used in our experiments. The average water vapour concentrations (as determined from four individual experiments) together with the response time of the reference humidity sensor are given in Table S5. Figure S16 shows a typical response curve of the reference sensor.

Table S5 Typical parameters for screening moisture-sensitive luminescent probes: average moisture content (ppm values calculated from dew points according to equations S2–S4) for the different steps and response times

T _{set}	Flow	Mixing ratio	Dew point	abs.	t ₉₀
(saturator)	[mL min ⁻¹]	[% water-	act	humidity	[min]
[°C]		saturated N ₂]	[°°]	[ppm]	
4.5	50*	100	2.4±0.03	7200	3
	100	64	-3.3±0.01	4610	3
	100	32	-11.4±0.04	2280	2
	100	16	-18.8±0.05	1140	3
	100	8	-25.9±0.05	580	3
	100	4	-32.7±0.08	280	3
	100	2	-38.2±0.20	160	8
	100	1	-44.4±0.71	80	15
	100	0	-54.1±0.38	23	56**

*To allow a more accurate dosage of smaller gas flows, the MFC device for water-saturated nitrogen had to be selected with a maximum flow of 50 mL min-¹.

**t10 for recoverage from 100% water-saturated nitrogen to the "zero gas"



Figure S16 Response curve of the capacitive reference dew point sensor during the standard test sequence.

Although working with much smaller gas flows than usually used (typical experiment setups for testing humidity sensors work with flows of 1 L/min or more),[13] concentrations, even in the trace range, are well reproducible. The generation of lower humidity concentrations, however, is rather difficult and could not be accomplished without more expensive equipment. Also, the "zero gas" (in our case, nitrogen 5.0 directly coming from a steel bottle (Linde) was used) would have to undergo further drying steps and equilibration times are very long once the ppm and sub-ppm concentration range is reached. [13]

In the datasheet for the reference used, a t_{90} value of 10 seconds going from -40 °C dew point to -20 °C dew point and a t_{90} of 80 seconds going from -20 °C to -40 °C are published. Thus, the longer response times in our measurements are most probably due to the rather small gas flow of 100 mL/min and the slow replacement of the nitrogen in the sensor cavity caused thereby. The observed additional increase (Table S6) in t_{90} values may be due to adsorption/desorption of the water vapour into the different matrix materials.

Mixing ratio [% water- saturated N ₂]	Dew point act [℃]	abs. humidity [ppm]*	t ₉₀ [min] Reference	Δφ [^σ] (t ₉₀ [min]) 1	∆ф [ீ] (t ₉₀ [min]) 2	Δφ [<i>°</i>] (t ₉₀ [min]) 3
0	-54	23	56**	-	-	-
1	-44	80	15	0.134 (7)	0.0912 (16)	-
2	-38	160	8	0.260 (4)	0.169 (13)	-
4	-33	280	3	0.493 (8)	0.294 (15)	-
8	-26	580	3	0.920 (19)	0.498 (13)	-
16	-19	1140	3	1.562 (18)	0.815 (16)	-
32	-11	2280	2	2.402 (16)	1.239 (13)	-
64	-3.3	4610	3	3.373 (12)	1.714 (8)	0.01 (n.d.)
100	2.4	7200	3	4.044 (4)	2.012 (2)	0.07 (n.d.)

Table S6: Response/Recovery times and $\Delta \phi$ values for dyes 1-3 in poly-5

*Calculated according to Eqs. S2-S4

**t₁₀ for recoverage from 100% water-saturated nitrogen to the "zero gas"

Temperature effects and cross-sensitivity

Temperature-dependence

Europium luminescence is known to be temperature-sensitive. Thus, sensitivity studies at different temperatures of the same blend sample ($Eu(TTA)_3 1$, 5wt% in *poly*-5) were carried out. Firstly, the phase shift of the sample was monitored at different measuring cell temperatures under a constant nitrogen flow of 100 mL/min.



Figure S17 Phase shift of a blend sample (Eu(TTA)₃ 1 in **poly-5**) at different temperatures

It can be seen that luminescence is temperature-dependent which makes thermostabilising of the measuring cavity essential. Also, virtually no drift of the sensor signal is noted.

To give a better idea about temperature cross sensitivity water vapour sensing curves were recorded at different temperatures. In Figure S19, the response curves of the same blend sample (**1** in **poly-5**) at different measuring cavity temperatures are compared.





At lower temperatures in the measuring cavity, a higher $\Delta\Phi$ value was observed for higher concentrations, but in the range of interest (0-1000 ppm), no significant improvement by lowering the temperature could be achieved. The absolute phase shift values differed temperature-dependently.

Additional matrix materials

Acetyl butyryl cellulose (*ABC*), hydroxypropyl cellulose (*HPC*) and poly(hydroxyethyl methacrylate) (*PHEMA*) polymers have been mentioned in publications about optochemical humidity sensors and were therefore used, together with polystyrene (*PS*) (often used in oxygen sensors due to its good gas permeability) as benchmarks for the norbornene-based polymers **poly-1-7** (structures of the corresponding monomers are given in Table S7).



Table S7: Alternative matrix materials



Figure S19 Sensitivity (phase shift difference vs. water vapour concentration in ppm) plots of **1** in different matrix materials

In terms of sensitivity, some of the norbornene-based materials are outperforming the commercially available matrix materials. For the poly(norbornenes) bearing ester and ether side groups, going from a methyl to an ethyl side chain is already reflected in a reduced sensitivity (*cf.* **poly-1** vs. **poly-3** and **poly-2** vs. **poly-4**) and it is even more pronounced for **poly-6** and **poly-7**. The main reason for this is that the fluorophores are hardly accessible by water when they are blended in a hydrophobic matrix. For a polar analyte like water, a good compromise between a large free volume and a certain degree of polarity to allow moisture ingress in the sensing layer has to be found.

References

- 1) H. E. Gottlieb, V. Kotlyar, and A. Nudelman, J. Org. Chem., 1997, 62, 7512.
- 2) Bruker AXS Programs: SMART, Version 5.629; SAINT, Version 6.45; SADABS, Version 2.10; XPREP, Version 6.14, Bruker AXS Inc., Madison, WI, USA, 2003.
- 3) G.M. Sheldrick, Acta Cryst., 2008 A 64 112.
- 4) N. M. Shavaleev, H. Adams, J. A. Weinstein, Inorganica Chimica Acta, 2007, 360, 700.
- 5) F. Niedermair, N. Noormofidi, C. Lexer, R. Saf, C. Slugovc, Polymer, 2011, 52, 1874.
- 6) Melby, L.R.;Rose, N.J.;Abramson, E.; Caris, J.C., J.Am.Chem.Soc., 1964, 86, 5117.
- 7) M. S. Sanford, J. A. Love, R. H. Grubbs, Organometallics, 2001, 20, 5314.
- 8) S. Niwayama, H. Cho, M. Zabet-Moghaddam, B. R. Whittlesey, *J. Org. Chem.*, 2010, **75**, 3775.
- R. O'Dell, D. H. McConville, G. E. Hofmeister, R. R. Schrock, J. Am. Chem. Soc., 1994, 116, 3414.
- 10) Trettnak, W., Kolle, C. Reininger, F., Dolezal, C., O'Leary, P., Sens. Actuators B Chem., 36, 506.
- 11) O. McGaughey, J. V. Ros-Lis, A. Guckian, A. K. McEvoy, C. McDonagh, B. D. MacCraith, *Anal. Chim. Acta*, 2006, **570**, 15.
- 12) R. Wernecke, Industrielle Feuchtemessung, Grundlagen, Messmethoden, technische Anwendungen, Wiley-VCH, Weinheim, **2003**
- 13) Venzke H., B. Schirmer, M. Still, A. Melling, F. Durst, Meas. Sci. Technol., 2000, 11, 1732.