Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Photoactive ultrathin molecular nanosheets with reversibly lanthanide binding terpyridine centers

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Synthesis of 4’-(2,2’:6’,2’’-terpyridine-4’-yl)-1,1’-biphenyl-4-thiol (TPBPT)

*4-(4-Methyl-2-thionyl)benzaldehyde (**1**)*

The synthesis was accomplished following a literature procedure.[1] In detail, 4-(methylthio)phenylboronic acid (759 mg, 4.5 mmol), 4-bromobenzaldehyde (924 mg, 4.98 mmol), Na_2CO_3 (954 mg, 9 mmol) and $Pd(OAc)_2$ (101 mg, 0.45 mmol) were placed in an oven-dry flask. THF (20 mL) was added and the reaction mixture was purged with N_2 whilst stirring. After refluxing for 16 h under inert conditions, further $Pd(OAc)_2$ (50 mg, 0.225 mmol) was added and refluxing was continued for 24 h. After cooling to room temperature, the precipitate was removed by filtration and the filtrate was diluted with CH_2Cl_2 (25 mL). After washing with water (3 × 50 mL) and brine (50 mL), the organic phase was separated and dried over Na_2SO_4. The drying agent was filtered off and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography [SiO_2, hexanes/diethyl ether (10:1 ratio) as eluent]. **1** was obtained as a pale-yellow solid (420 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, CHO, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 2.57 (s, SCH_3, 3H) ppm.

*4'-(4'-(Methylthio)-[1,1'-biphenyl]-4-yl)-2,2':6',2''-terpyridine (**2**)*

Following the general protocol for the synthesis of 4’-aryl-substituted 2,2':6',2''-terpyridines,[2] **2** was synthesized by dissolving **1** (420 mg, 1.84 mmol), 2-acetylpyridine (446 mg, 3.7 mmol) and NaOH (62 mg) in a mixture of aq. NH_3 (25%, 1 mL) and ethanol (5 mL). The reaction mixture was stirred for 15 h at 50 °C. After cooling to room temperature, the precipitate was filtered off, washed with cold methanol (2 mL) and dried in *vacuo*. Compound **2** was obtained as an off-white solid (500 mg, 80%) which needed no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 2H), 8.78 (m_c, 2H) 8.72 (br d, J = 7.9 Hz, 2H), 8.03 (br d, J = 8.5 Hz, 2H), 7.93 (td, J = 7.6 Hz, 1.7 Hz, 2H), 7.76 (br d, J = 8.5 Hz, 2H), 7.64 (br d, J = 8.4 Hz, 2H), 7.40 (br d, J = 8.2 Hz, 2H), 7.39 (m_c, 2H), 2.58 (s, SCH_3, 3H) ppm.

*4'-([2,2':6',2''-Terpyridine]-4'-yl)-[1,1'-biphenyl]-4-thiol (**3**)*

A suspension of **2** (500 mg, 1.41 mmol) and KO^{t}Bu (1.19 g, 10.61 mmol) in DMF (10 mL) was purged with N_2. After the addition of *tert*-butylthiol (0.8 mL, 7.1 mmol), the reaction mixture was heated to 100 °C for 15 h. After cooling to room temperature, the dark brown solution was added to a sat. aq. NH_4Cl solution (75 mL). The grey-brown precipitate was filtered off and dried *in vacuo* to afford **3** (375 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 3H), 8.68 (d, *J* = 4.8 Hz, 2H), 8.62 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.83 (t, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30 (m_c, 2H), 3.46 (s, SH, 1H) ppm.

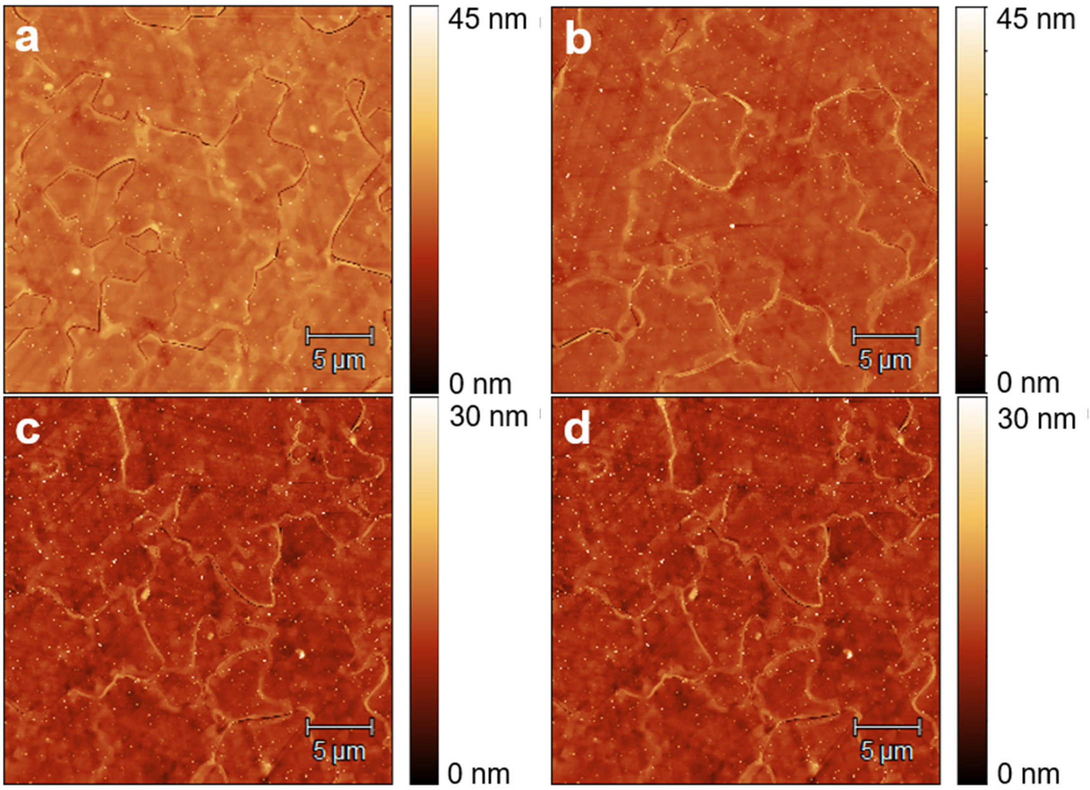

Figure S1. 30×30 µm^2 AFM topography images of pure TPBPT SAM (a), TPBPT SAM after coordination with Eu (b), TPBPT CNM coordinated with Eu after cross-linking (c), and TPBPT CNM coordinated with Eu before cross-linking (d) grown on Au/mica. For all samples calculated roughness (root mean square, RMS) for the whole images are 2.0 +/- 0.2 nm, for 4 x 4 µm cutouts are 1.2 +/- 0.3 nm.

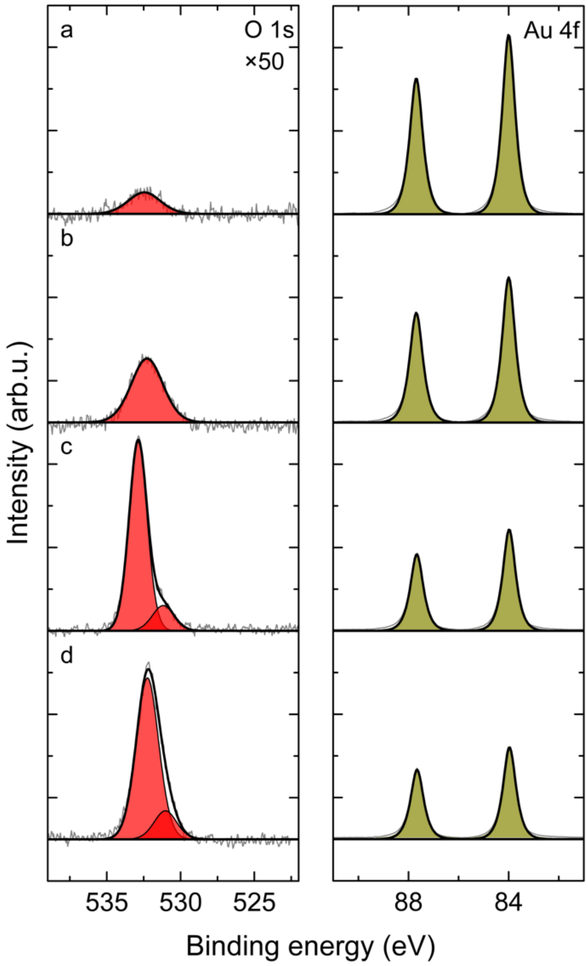

Figure S2. O 1s and Au 4f XP spectra of the TPBPT SAM (a), TPBPT-BPT SAM (b), TPBPT CNM (c) and TPBPT-BPT CNM (d) on Au. Note that the spectra in (a) and (b) were measured using 600 W power of the X-ray source; whereas, the spectra in (c) and (d) were measured using 300 W.

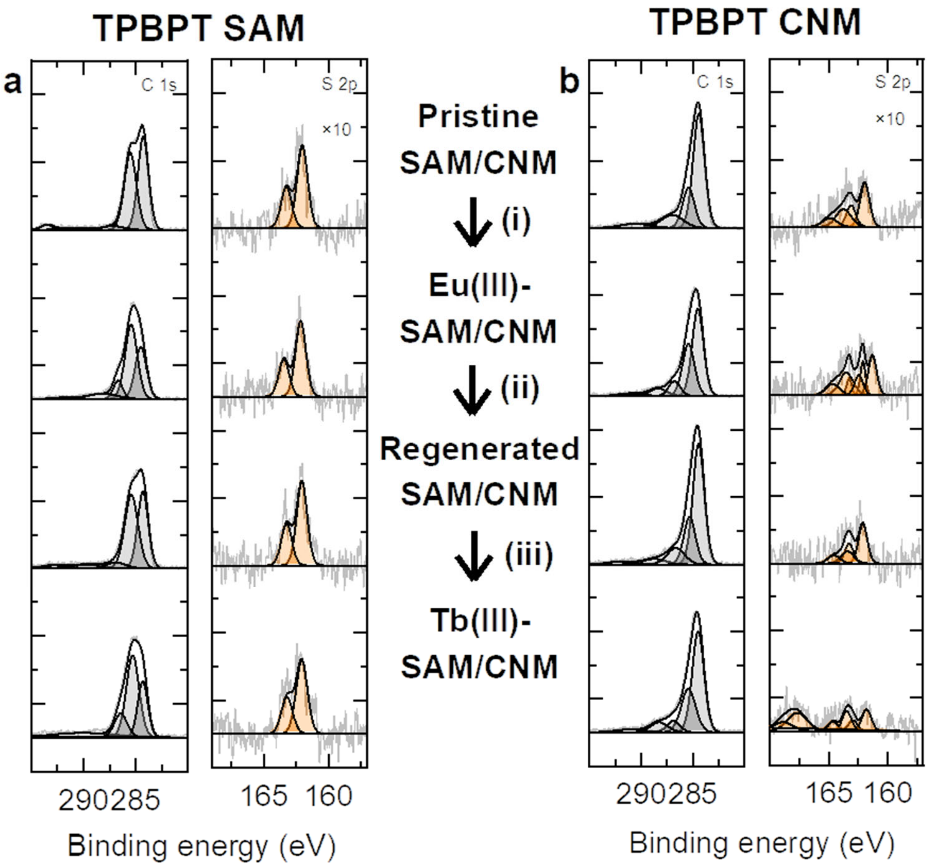

Figure S3. C 1s and S 2p XP spectra of the following subsequent steps: (i) Complexation with Eu(III) ions, (ii) regeneration with EDTA, (iii) complexation with Tb(III) for the TPBPT SAM (a) and the TPBPT CNM (b).

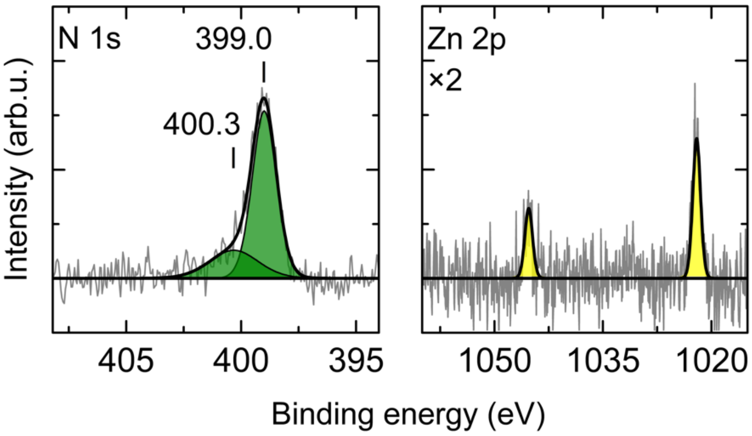

Figure S4. N 1s and Zn 2p XP spectra of the TPBPT SAM rinsed with EDTA and ultrapure water

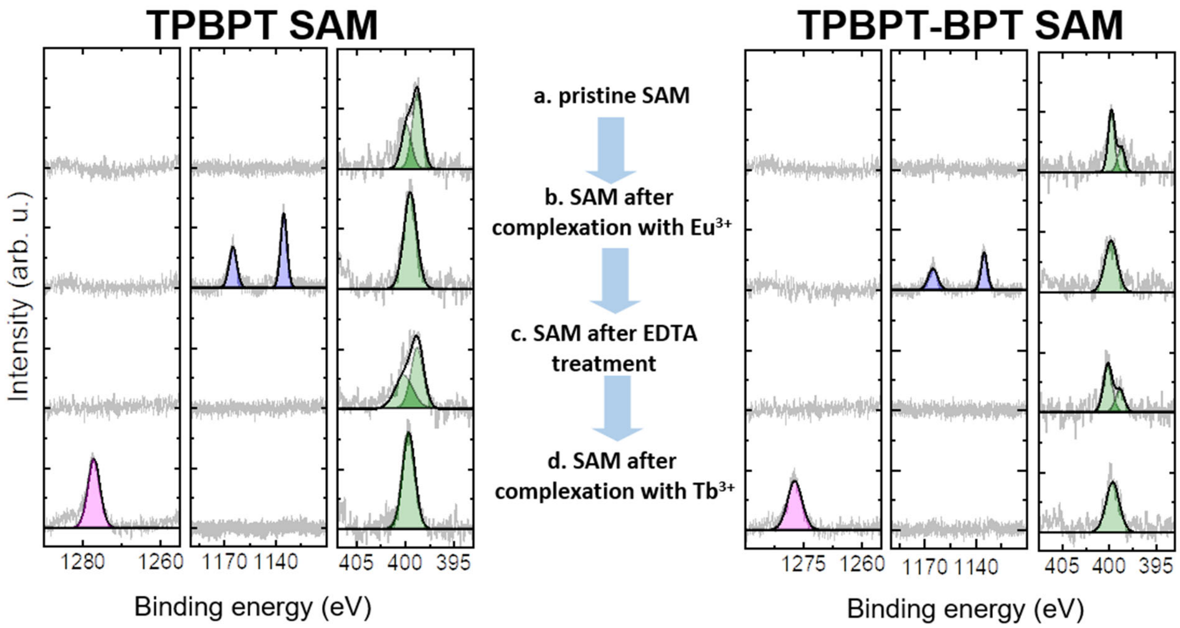

Figure S5. XP Tb $3d_{3/2}$, Eu 3d and N 1s spectra of the lanthanide complexation to TPBPT and TPBPT-BPT SAMs using 300 W power of the X-ray source and presented on the same intensity scale.

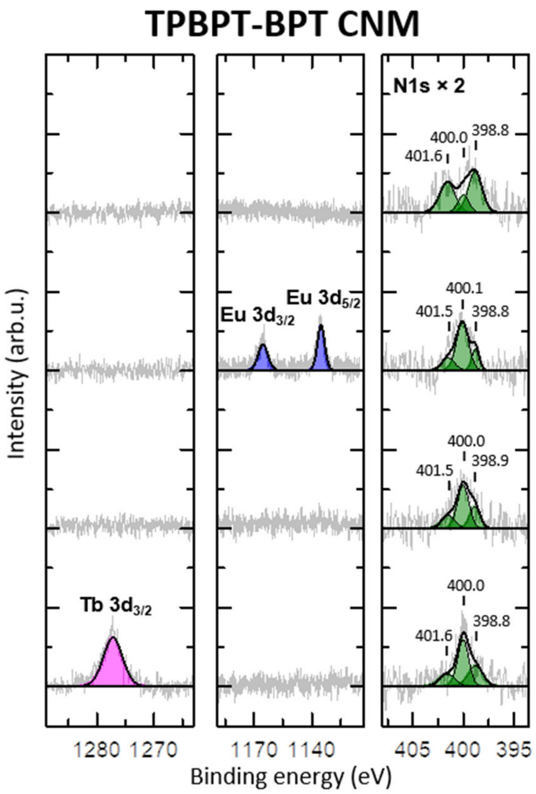

Figure S6. XP spectra of the lanthanide complexation/regeneration cycles of a TPBPT-BPT CNM conducted similarly as in Figure S3.

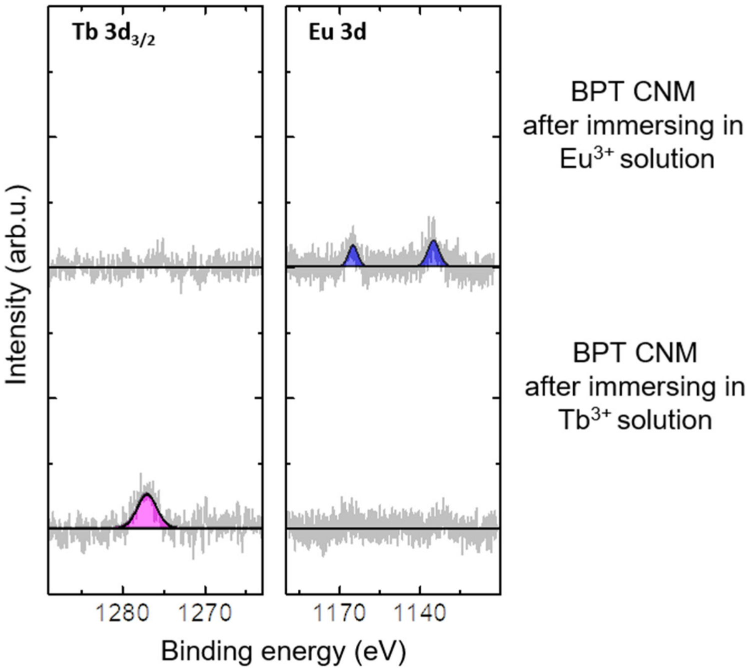

Figure S7. XP spectra of a BPT CNM showing some non-specific lanthanide attachment measured using 300 W power of the X-ray source and presented at the same intensity scale as for TPBPT CNM in Figure 3b.

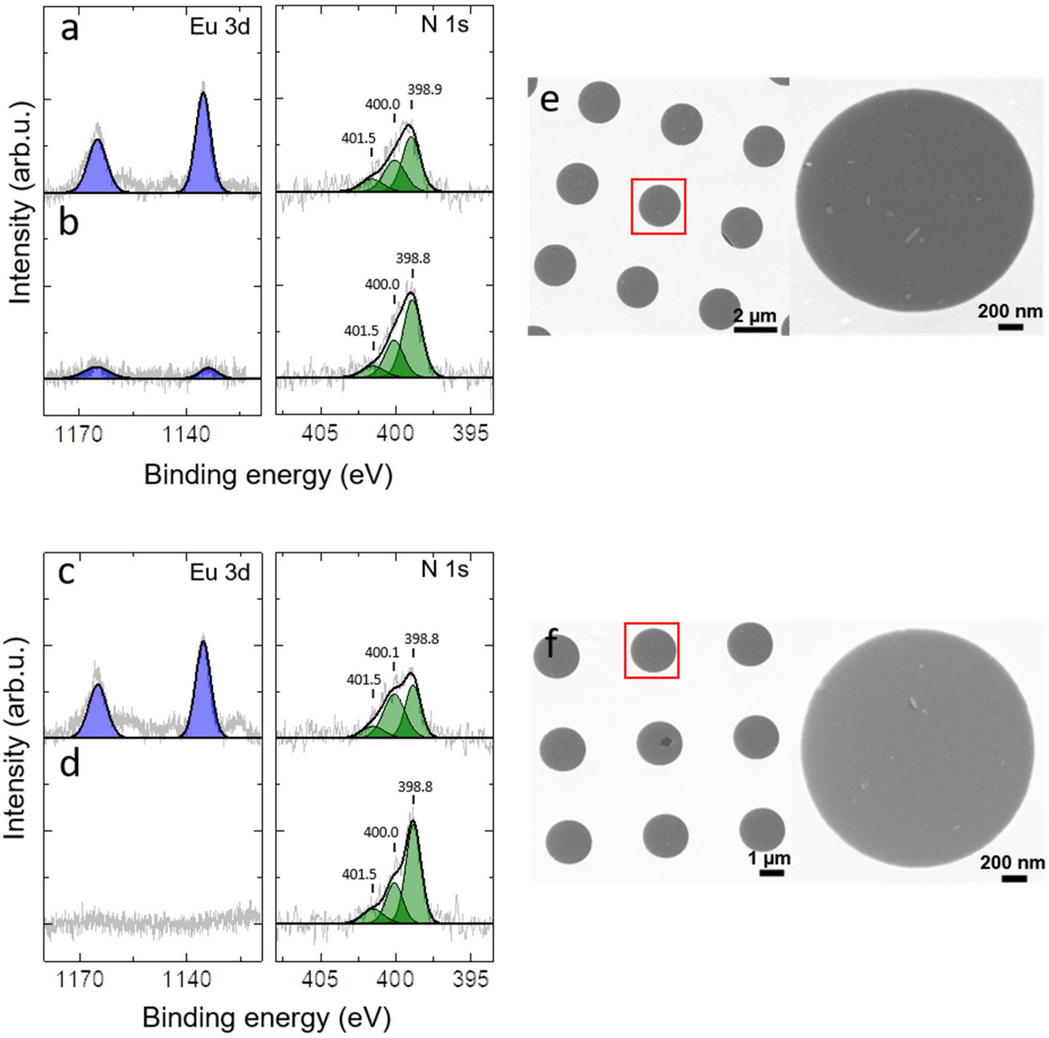

Figure S8. XP spectra of the TPBPT CNMs coordinated with Eu(III) before (a) and after (c) cross-linking as well as after rinsing with EDTA (b and d). SEM images TPBPT CNMs transferred onto the TEM grids. The CNM were coordinated with Eu(III) in (e) before and in (f) after the cross-linking.

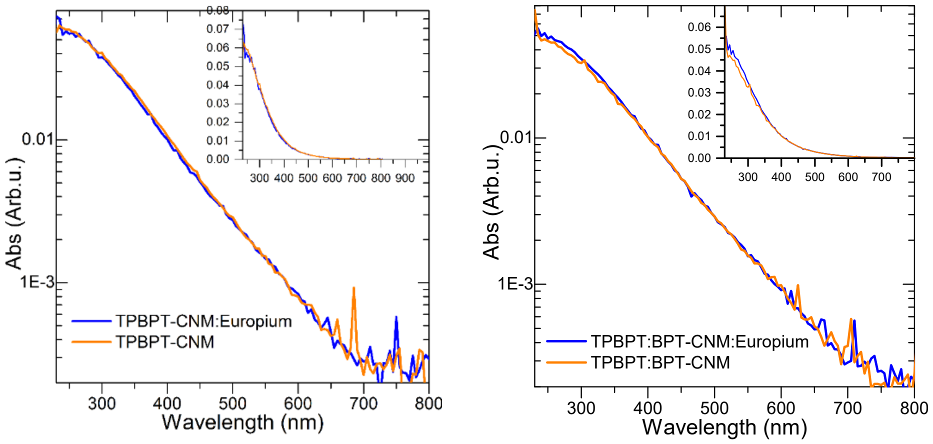

Figure S9. PDS absorption measurements data for pure and coordinated with europium TPBPT and TPBPT-BPT CNMs.

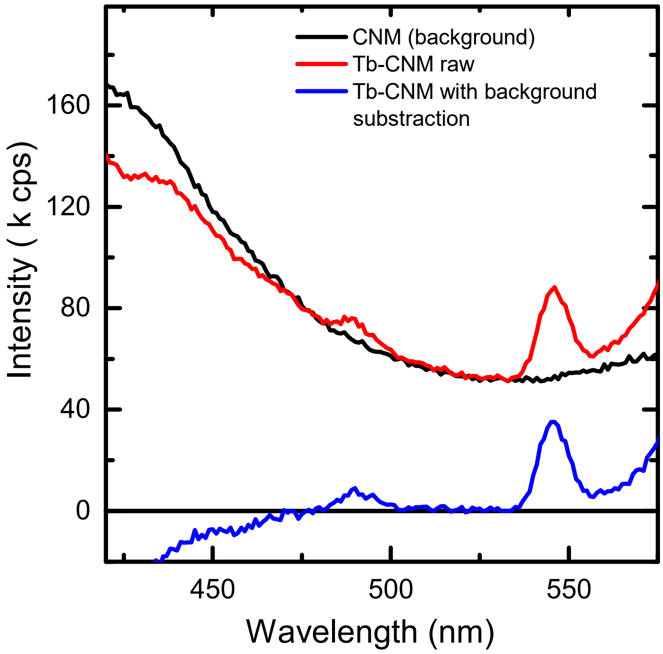

Figure S10 . The photoluminescence data with the background signal for pure and coordinated with Tb(III) TPBPT CNM.

Table S1. Quantitative analysis of the high-resolution XP spectra of the TPBPT and TPBPT-BPT SAMs, TPBPT CNM and TPBPT-BPT CNMs on Au presented in Figure 2 including the peak assignment, binding energies, full width at half maximum (FWHM) values and areas (in %) obtained from the spectra deconvolution. The peak fitting of the sulfur doublet was performed using fixed intensity ratios due to the spin-orbit coupling of the p-photoelectrons. For the elemental ratios mentioned in the main paper the relative sensitivity factors (RSF) of 1 for C 1s, 1.8 for N 1s, 2.9 for O 1s and 1.11 for S $2p_{3/2}$ were used.[3]

Peak assignment	Binding energy, eV	FWHM, eV	Area, %
TPBPT SAM			
N 1s			
Pyridyl N	398.9	1.2	80
Weakly interacting pyridyl N	399.8	1.6	20
C 1s			
C-C aromatic	284.3	1.2	48
C-S/C-N	285.5	1.4	45
Aromatic shake-up / oxidized carbon	287.2	2.5	4
Aromatic shake-up	291.0	3.0	3
S $2p_{3/2,\ 1/2}$			
Thiolate	162.0, 163.2	1.0	100
O 1s			
C-O / C-OH	532.5	2.6	100
TPBPT-BPT SAM			
N 1s			
Pyridyl N	398.7	1.8	39
Weakly interacting pyridyl N	399.8	1.1	61
C 1s			
C-C aromatic	284.3	1.3	55

C-S/C-N	285.2	1.7	30
Aromatic shake-up / oxidized carbon	286.7	2.5	11
Aromatic shake-up	290.5	2.5	4
S 2p$_{3/2,\ 1/2}$			
Thiolate	162.0, 163.2	1.1	100
O 1s			
C=O	531.2	1.7	14
C-O / C-OH	532.9	1.4	86
TPBPT CNM			
N 1s			
Pyridyl N	398.7	1.3	66
Weakly interacting pyridyl N / amines / pyrrols	400.1	1.3	23
Protonated pyridyl N	401.4	2.0	11
C 1s			
C-C aromatic	284.4	1.3	59
C-S/C-N	285.4	1.3	21
Aromatic shake-up / oxidized carbon	287.0	2.5	13
Aromatic shake-up	290.6	3.5	6
S 2p$_{3/2,\ 1/2}$			
Thiolate	161.9, 163.1	0.9	50
Disulfide / Thiol	163.7, 164.9	1.5	50
O 1s			
C-O / C-OH	532.3	2.5	100
TPBPT-BPT CNM			
N 1s			
Pyridyl N	398.8	1.6	46
Weakly interacting pyridyl N / amines / pyrrols / azo-groups	400.0	1.2	16

Protonated pyridyl N	401.6	1.8	38
C 1s			
C-C aromatic	284.3	1.3	67
C-S/C-N	285.6	1.8	17
Aromatic shake-up / oxidized carbon	287.1	2.5	12
Aromatic shake-up / highly oxidized carbon	289.2	2.5	4
S 2p$_{3/2,\ 1/2}$			
Thiolate	161.8, 163.0	1.5	59
Disulfide / Thiol	163.2, 164.4	1.0	41
O 1s			
C=O	531.0	1.8	15
C-O / C-OH	532.2	1.8	85

Table S2. Quantitative analysis of the high-resolution N 1s, Eu 3d and Tb $3d_{3/2}$ XP spectra of the TPBPT SAM, and TPBPT CNM coordinated with lanthanides and regenerated with EDTA presented in Figure 3 including the peak assignment, their binding energies, full width at half maximum (FWHM) values and areas (in %) obtained from the spectra deconvolution. For the elemental ratios mentioned in the main paper the relative sensitivity factors (RSF) of 1.8 for N 1s, 43.2 for Eu $3d_{5/2}$ and 19.77 for Tb $3d_{3/2}$ were used.[3]

Peak assignment	Binding energy, eV	FWHM, eV	Area, %
TPBPT SAM + Eu			
N 1s			
Weakly interacting pyridyl N	399.9	1.7	100
Eu 3d			
Eu^{3+} ($3d_{5/2}$)	1135.4	5.0	100
Eu^{3+} ($3d_{3/2}$)	1165.0	6.0	
Regenerated TPBPT SAM			
N 1s			
Pyridyl N	399.0	1.1	65
Weakly interacting pyridyl N	400.0	1.7	35
TPBPT SAM + Tb			
N 1s			
Weakly interacting pyridyl N	399.7	1.8	100
Tb $3d_{3/2}$			
Tb^{3+}	1277.1	3.2	100
TPBPT CNM + Eu			
N 1s			
Pyridyl N	398.8	1.2	41
Weakly interacting pyridyl N / amines / pyrrols / azo-groups	400.1	1.7	47
Protonated pyridyl N	401.5	1.8	12

Eu 3d			
Eu^{3+} ($3d_{5/2}$)	1135.4	5.0	100
Eu^{3+} ($3d_{3/2}$)	1165.0	6.0	
Regenerated TPBPT CNM			
N 1s			
Pyridyl N	398.8	1.2	61
Weakly interacting pyridyl N / amines / pyrrols	400.0	1.3	26
Protonated pyridyl N	401.5	1.7	13
TPBPT CNM + Tb			
N 1s			
Pyridyl N	398.7	1.3	53
Weakly interacting pyridyl N / amines / pyrrols	400.1	1.7	38
Protonated pyridyl N	401.6	1.2	9
Tb $3d_{3/2}$			
Tb^{3+}	1277.0	4.5	100

SUPPORTING REFERENCES

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2. J. H. Wang and G. S. Hanan, *Synlett.*, 2005, **2005**, 1251-1254.
3. J. H. Scofield, *J. Electron. Spectros. Relat. Phenomena*, 1976, **8**, 129-137.