Luminescent (metallo-supramolecular) cross-linked lanthanide hydrogels from a btp (2,3-bis(1,2,3- triazol-4-yl)picolinamide) monomer give rise to strong Tb(III) and Eu(III) centred emissions

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ESI

General

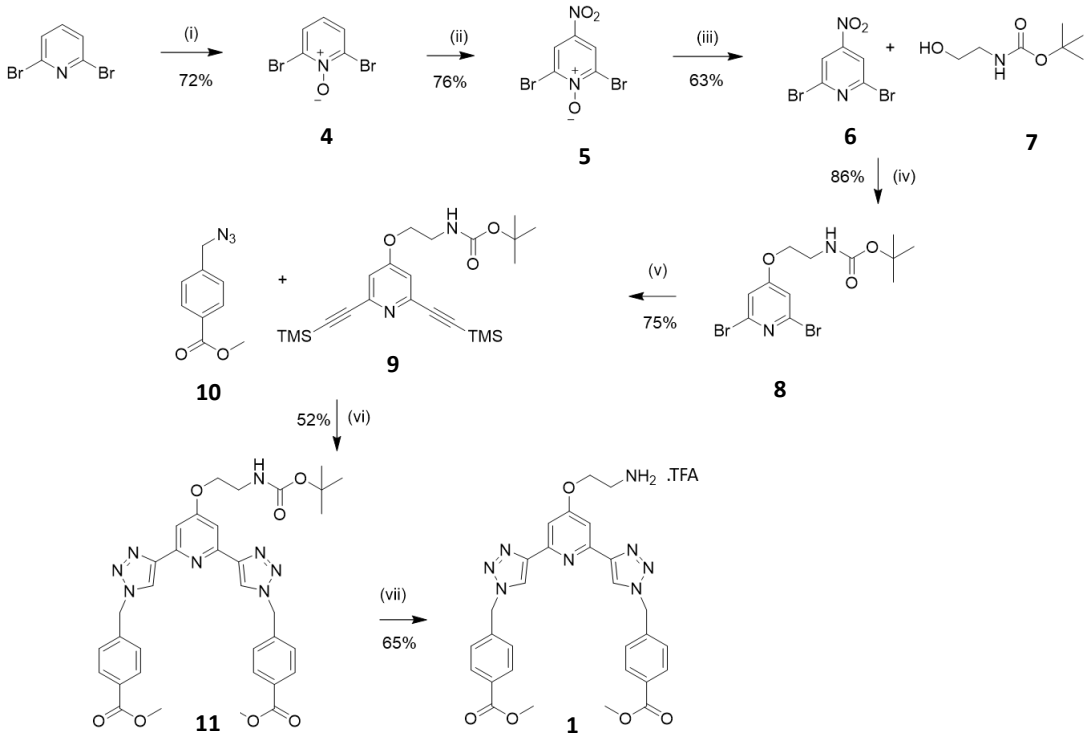
NMR spectroscopy: NMR spectra were recorded on a Bruker DPX-400 Avance spectrometer at frequencies of 400.13 MHz and 100.6 MHz for ^{1}H NMR and ^{13}C NMR respectively or Bruker-AV-600 spectrometer at frequencies of 600.13 MHz and 150.2 MHz for ^{1}H NMR and ^{13}C NMR respectively. All spectra were recorded in commercially available deuterated solvents and the residual proton signals of those solvents were used as a reference with chemical shifts expressed in parts per million (ppm).

Mass spectrometry: Mass spectrometry was carried out in the School of Chemistry, Trinity College Dublin. Electrospray mass spectra were measured ona Micromass LCT spectrometer calibrated against a leucine enkephaline standard and MALDI A-ToF mass spectra were obtained on a MALDI A-TOF Premier and high-resolution mass spectrometry was performed using Glu-Fib as an internal reference (m/z = 1570.677).

X-ray Crystallography (General description): Structural and refinement parameters are presented below in tabulated form for structures **6** and **1**. X-ray crystallographic data were collected in-house by Dr. June Lovitt using a Brucker APEX-II Duo dual-source instrument and using graphite-monochromated Mo K α (λ = 0.71073 A) or microfocus Cu Kα (λ = 1.54178 A) radiation. Datasets were collected using ω and φ scans and the samples were immersed in oil. Brucker APEX suite of programs were used to reduce and process the data. Multi-scan absorption corrections were applied using SADABS. The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI. The functions minimized were

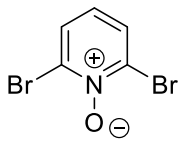
$\Sigma w(F^2_o-F^2_c)$, with $w=[\sigma^2(F^2_o)+aP^2+bP]^{-1}$, where $P=[\max(F_o)^2+2F^2_c]/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. In cases where U_{ij} or position restraints were necessary, these were employed as sparingly as possible and only for the purpose of maintaining chemically sensible geometries and ADPs.

Synthesis



Scheme S1. *Synthesis and structure of* ***11*** *and* ***1****. Reagents and conditions: (i) TFA, H_2O_2, 100 ˚C (ii) H_2SO_4, HNO_3, 60 ˚C (iii) PBr_3, $CHCl_3$, (iv) Na, THF (v) CuI, $Pd(PPh_3)_4$, TMS-acetylene, DMF:NEt_3 (vi) $CuSO_4.5H_2O$, K_2CO_3, sodium ascorbate, DMF:H_2O (4:1) (vii) TFA (see main article).*

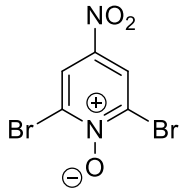
2,6-Dibromopyridine 1-oxide (4)



Synthesised according to literature procedure[1] from 2,6-dibromopyridine (2.0 g, 8.44 mmol) was dissolved in TFA (15 mL, 0.196 mmol) and hydrogen peroxide (2 mL) and the mixture was heated to reflux for 48 hours. The resulting solution was diluted in H_2O and stirred for one hour, after which the starting material was filtered off as a pale pink solid. The yellow filtrate was extracted into CH_2Cl_2 (3 x 20 mL) and the organic layer was washed with K_2CO_3 (0.5

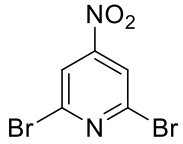
M, 3 x 10 mL). The organic layer was then dried over $MgSO_4$, and concentrated under reduced pressure to yield a pale yellow solid (1.533 g, 72%); m.p. 155 - 158 ºC; HRMS (*m/z*) (ESI+): $C_5H_3NOBr_2^+$ *m/z* = 250.8581 $[M+H]^+$. Found *m/z* = 251.8510; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.65 (d, *J* = 8.1 Hz, 2H, *meta*-H), 6.96-6.88 (t, *J* = 8.1 Hz, 1H, *ortho*-H); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 132.8, 130.2, 125.9; IR ν_{max} (cm^{-1}): 3109, 3085, 2495, 1930, 1863, 1795, 1667, 1577, 1526, 1436, 1359, 1250, 1156, 1134, 1109, 1074, 836, 761, 744;

2,6-Dibromo-4-nitropyridine 1-oxide (5)



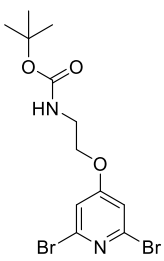
Synthesised according to literature procedure[2] from **4** (1.3g, 5.3 mmol) and concentrated H_2SO_4 (8.5 mL) in HNO_3 (3.5 mL). The mixture was stirred at 80 ˚C overnight and upon cooling to room temperature was poured onto ice. The mixture was neutralised with ammonium hydroxide and the product was filtered off as a pale yellow solid (1.216 g, 76%); m.p. 169 - 173 ºC; HRMS (*m/z*) (ESI+): $C_5H_3N_2O_3Br_2^+$ *m/z* = 295.8432 $[M+H]^+$. Found *m/z* = 296.8505; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 2H), ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 133.5, 123.9 ; IR ν_{max} (cm^{-1}): 3345, 2971, 1515, 1465, 1408, 1380, 1325, 1282, 1150, 1129, 1107, 948, 911, 884, 816, 761, 733, 709;

2,6-Dibromo-4-nitropyridine (6)



Synthesised according to literature procedure[3] from **5** (1.44 g, 4.8 mmol) in with acetic acid (40 mL, 69.0 mmol) and Fe filings (1.06 g, 19.0 mmol) to yield a light brown solid (0.82 g, 63%);HRMS (*m/z*) (ESI+): $C_5H_3N_2O_3Br_2^+$ *m/z* = 295.8432 $[M+H]^+$. Found *m/z* = 296.8505; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.19 (s, 2H), ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 142.5, 120.6; IR ν_{max} (cm^{-1}):3251, 3245, 2549, 1758, 1743, 1622, 1528, 1438, 1358, 1253, 1112, 1012, 1009, 943, 766, 748. This compound was also characterised in the solid state using X-ray crystallography as shown below.

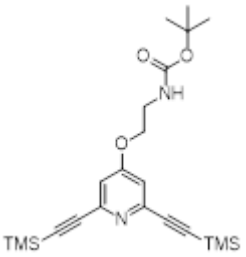
(((2,6-Dibromopyridin-4-yl)oxy)ethyl)tert-butyl carbamate (8)



7 (1.38 g, 4.90 mmol) was dissolved in dry THF and sodium (0.176 g, 7.35 mmol) was added. The mixture was stirred under argon for 3 hours. Compound **6** was then dissolved in THF and added. The mixture was stirred at room temperature for 24 hours. The reaction was quenched with a saturated solution of ammonium chloride, diluted in 50 mL water

and extracted into ethyl acetate. The solution was dried over magnesium sulphate and the solvent was removed under reduced pressure. The product was purified by flash column chromatography (Pet Ether: Ethyl Acetate; to 90:10) to yield an orange oil. (1.383 g, 3.49 mmol, 60 %). m.p. 163 - 168 ºC; HRMS (*m/z*) (ES-): Calculated for $C_{12}H_{16}Br_2N_2O_3Cl^-$ *m/z* = 428.9216 $[M+Cl]^-$. Found *m/z* = 428.9228 ; ^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.98 (s, 2H, pyr H), 4.89 (s, 1H, NH), 4.07 (t, *J* = 4.1 Hz, 2H, O-CH_2), 3.53 (q, *J* = 4.1 Hz, 2H, N-CH_2), 1.45 (s, 9H, t-butyl). ^{13}C NMR (150 MHz, DMSO): δ = 166.6, 155.7, 141.2, 113.8, 80.0, 68.2, 39.6, 28.4.; IR ν_{max} (cm^{-1}): 2976, 1695, 1569, 1532, 1366, 1280, 1235, 1151, 1067, 1041, 957, 760

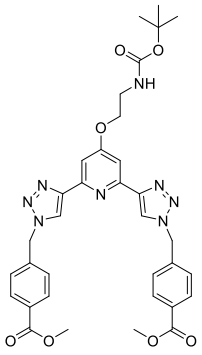
tert-Butyl (2((2,6-bis((trimethylsilyl)ethynyl)pyridine-4-yl)oxy)ethyl)carbamate (9)



Ligand **8** (1.18 g, 2.98 mmol), $Pd(PPh_3)_2Cl_2$ (0.126 g, 0.18 mmol) and CuI (0.039 g, 0.36 mmol) were suspended in dry THF:NEt_3 under argon atmosphere over ice. Ethynyltrimethylsilane (1 mL, 7.45 mmol) was added dropwise and the reaction was stirred at room temperature for 48 hours. The reaction mixture was concentrated under reduced pressure and suspended in hexane. The suspension was filtered through celite and purified by flash chromatography (Pet Ether: Ethyl Acetate) to yield a brown oil. (0.834 g, 1.94 mmol, 65 %). m.p. 172 - 178 ºC; HRMS (*m/z*) (ESI+): Calculated for $C_{22}H_{35}N_2O_3Si_2^+$ *m/z* = 431.2186 $[M+H]^+$. Found *m/z* = 431.2105 ; ^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.93 (s, 2H, pyridine H), 4.89 (s, 1H, NH), 4.08 (t, *J* = 4.1 Hz ,2H, O-CH_2), 3.53 (q, *J* = 4.1 Hz, 2H, N-CH_2), 1.45 (s, 9H, O-$(CCH_3)_3$), 0.25 (s, 18H, TMS).^{13}C NMR (150 MHz, DMSO): δ = 165.2, 152.9, 144.0, 113.7, 102.4, 80.0, 67.8, 39.9, 29.9, 28.5, -0.3; IR ν_{max} (cm^{-1}): 3821, 2963, 2166, 1693, 1580, 1530, 1339, 1272, 1245, 1153, 1048, 842, 759.

Dimethyl 4,4'-(((4-(2-((tert-butoxycarbonyl)amino)ethoxy)pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene))dibenzoate (11)

To a solution of 4-bromomethyl benzoate (**10**) (0.954 g, 4.17 mmol) in 10 mL 4:1 DMF/water was added sodium azide (0.271 g, 4.17 mmol) and the reaction mixture was stirred for one hour to yield the azide intermediate which was not isolated and therefore used without further purification. To this solution was added **9** (0.897 g, 2.08 mmol), $CuSO_4.5H_2O$ (0.208 g, 0.83 mmol), sodium ascorbate (0.329 g,



1.67 mmol) and anhydrous K_2CO_3 (0.575 g, 4.16 mmol) and stirred at room temperature under argon atmosphere overnight. 1 M EDTA/NH_4OH solution was added to the mixture and the product was extracted into CH_2Cl_2. The organic layer was washed with water and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield an off-white solid. (0.724 g, 1.08 mmol, 52 %). The product decomposed over 242 °C. HRMS (*m/z*) (ESI+): Calculated for $C_{34}H_{36}N_8O_8H^+$ *m/z* = 669.2785 $[M+H]^+$. Found *m/z* = 669.2785 ; ^{1}H NMR (600 MHz, DMSO) δ = 8.69 (s, 2H, triazole H), 7.98 (d, *J* = 8.2 Hz, 4H, Ar *H*-COOMe), 7.49 (s, 2H, pyr H), 7.45 (d, *J* = 8.2 Hz, 4H, Ar *H*-CH_2), 7.06 (s, 1H, NH), 5.80 (s, 4H, C*H*$_2$-Ar), 4.21 (t, *J* = 5.6 Hz, 2H, O-C*H*$_2$), 3.84 (s, 6H, O-CH_3), 3.37 (q, *J* = 5.6 Hz, 2H, C*H*$_2$-NH), 1.37 (s, 9H, O$(CH_3)_3$). ^{13}C NMR (150 MHz, DMSO): δ = 170.3, 166.3,151.3, 146.6, 138.6, 130.5, 130.2, 129.0, 128.2, 128.1, 108.4, 77.2, 69.9, 54.2, 52.3, 39.5, 28.4.; IR ν_{max} (cm^{-1}): 3099, 2952, 1689, 1563, 1536, 1499, 1396, 1270, 1171, 3099, 2236, 1717, 1407, 1368, 1110, 1046, 1022, 936, 850, 767, 725.

Figures

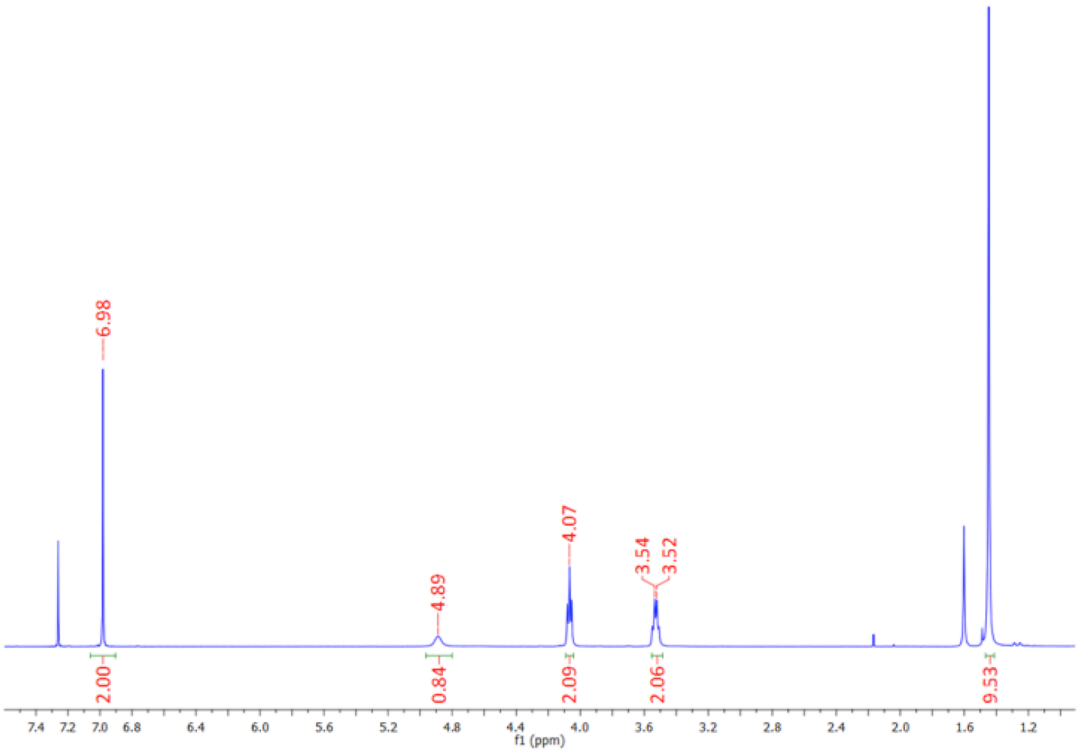


Figure S1 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **8.**

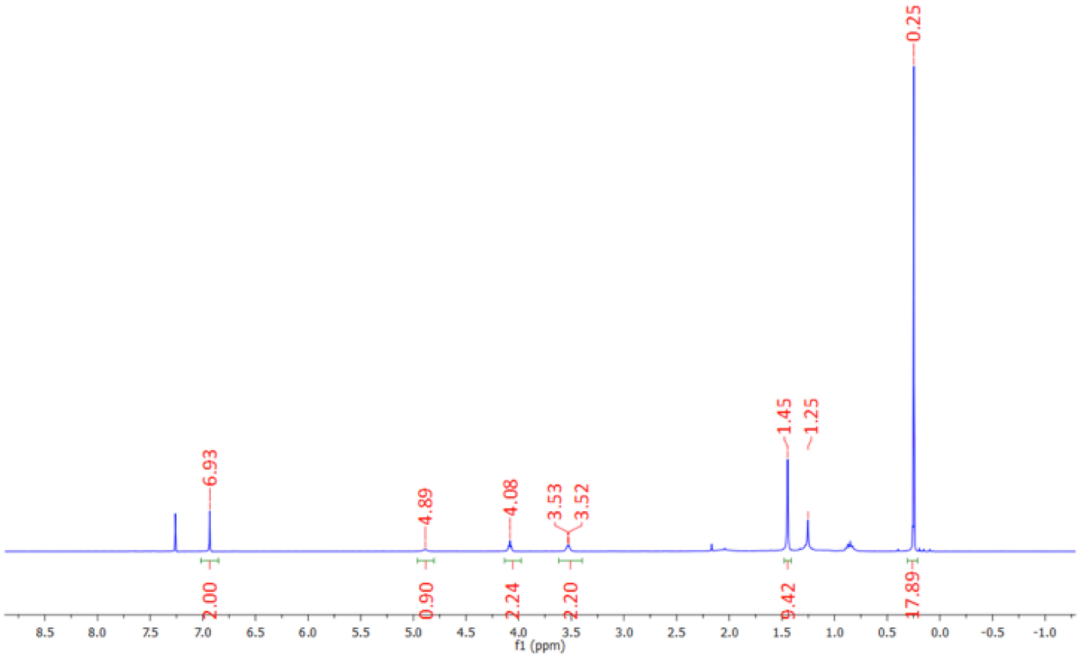


Figure S2 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **9**.

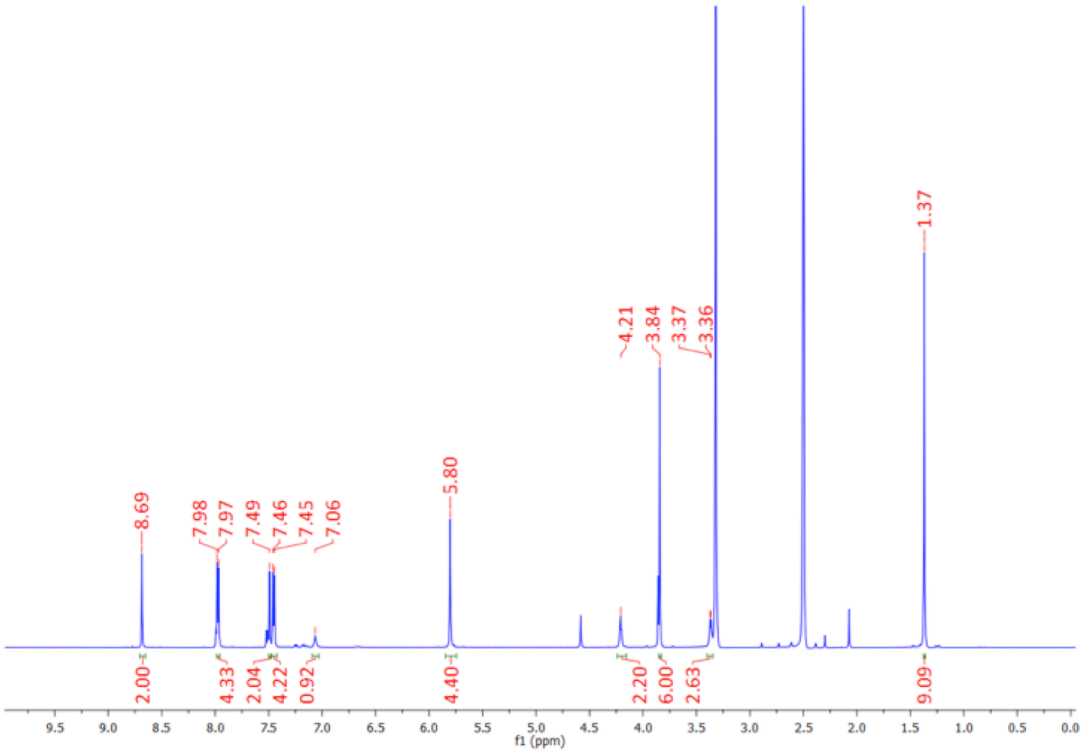


Figure S3 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **11**.

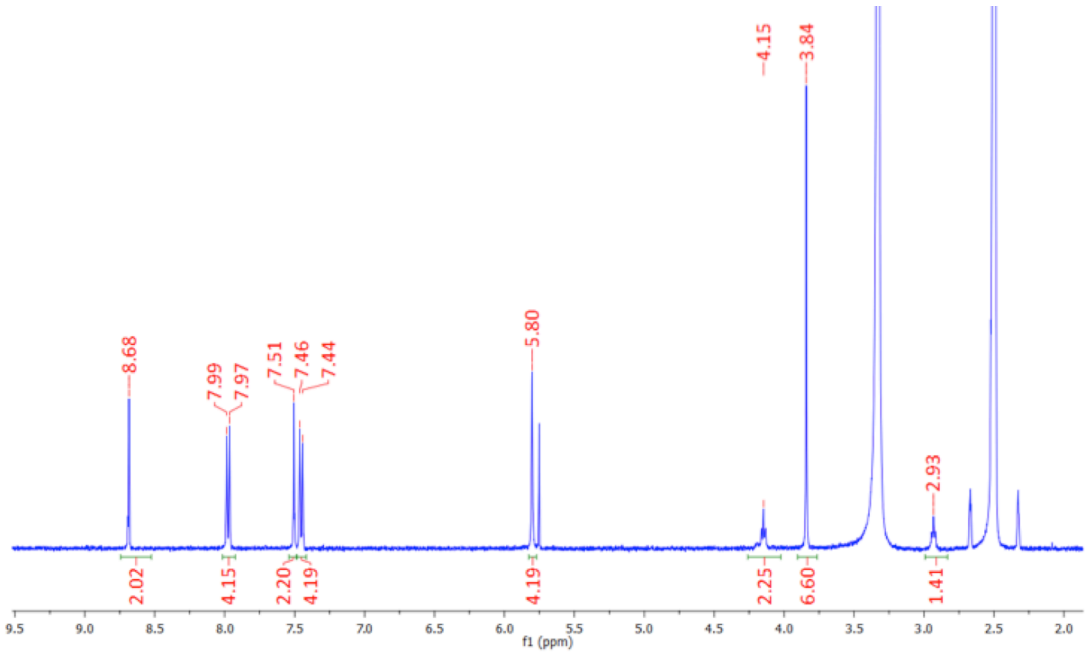


Figure S4 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **1**.

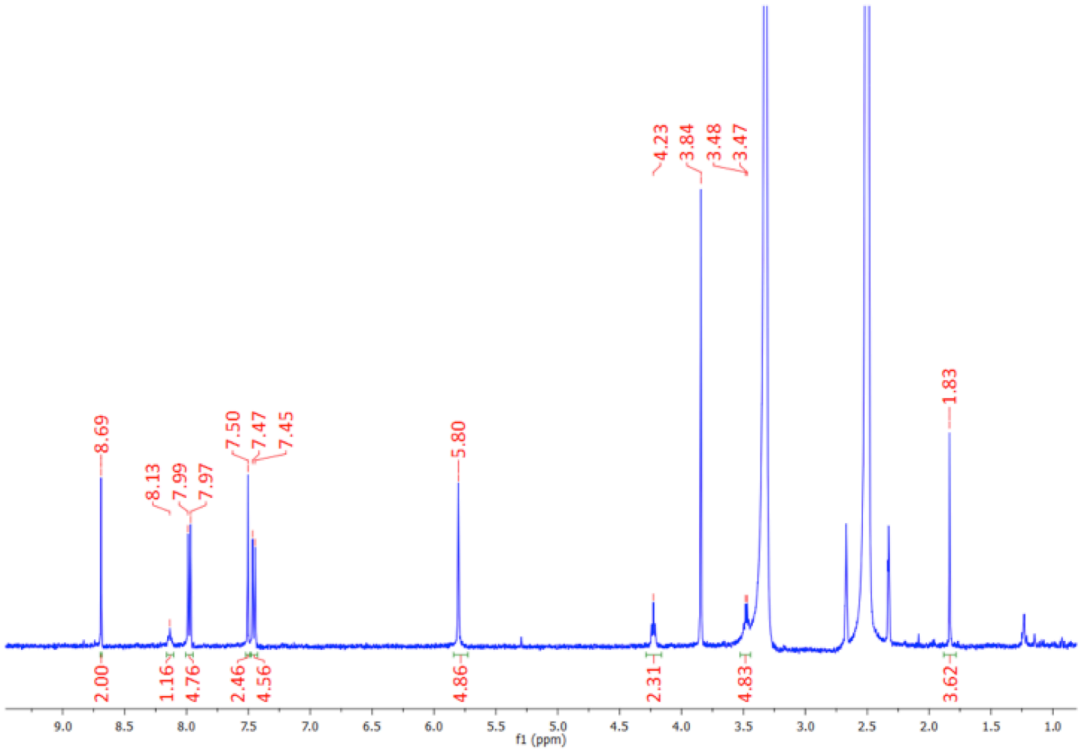


Figure S5 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **2**.

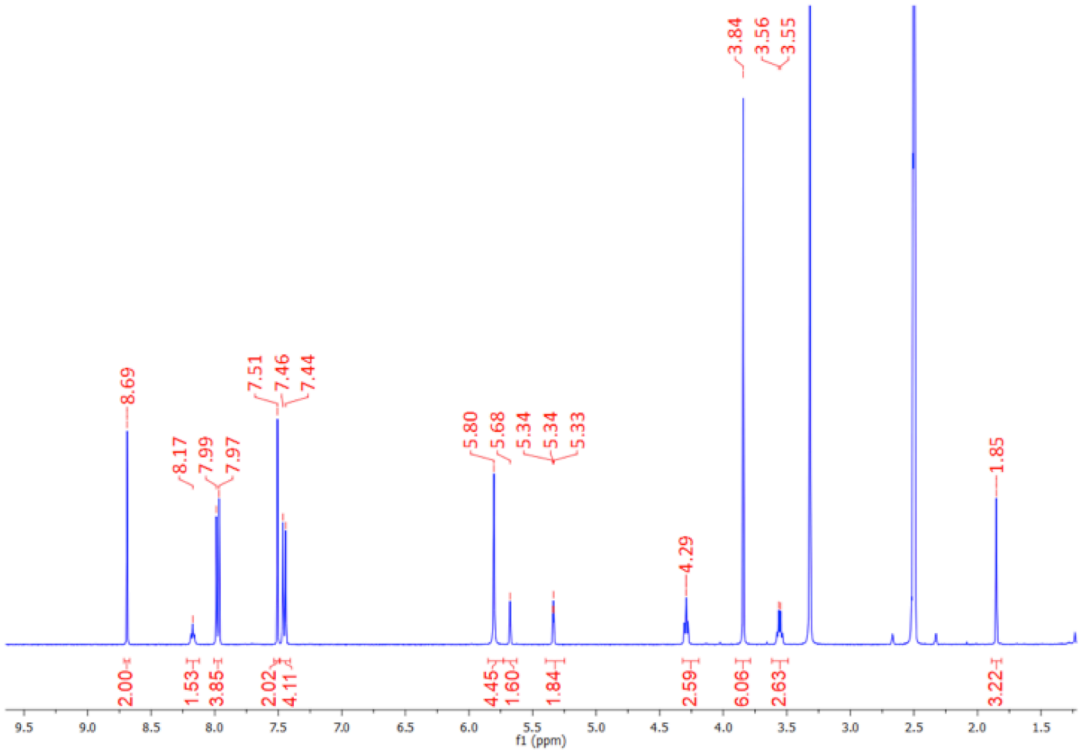


Figure S6 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **3**.

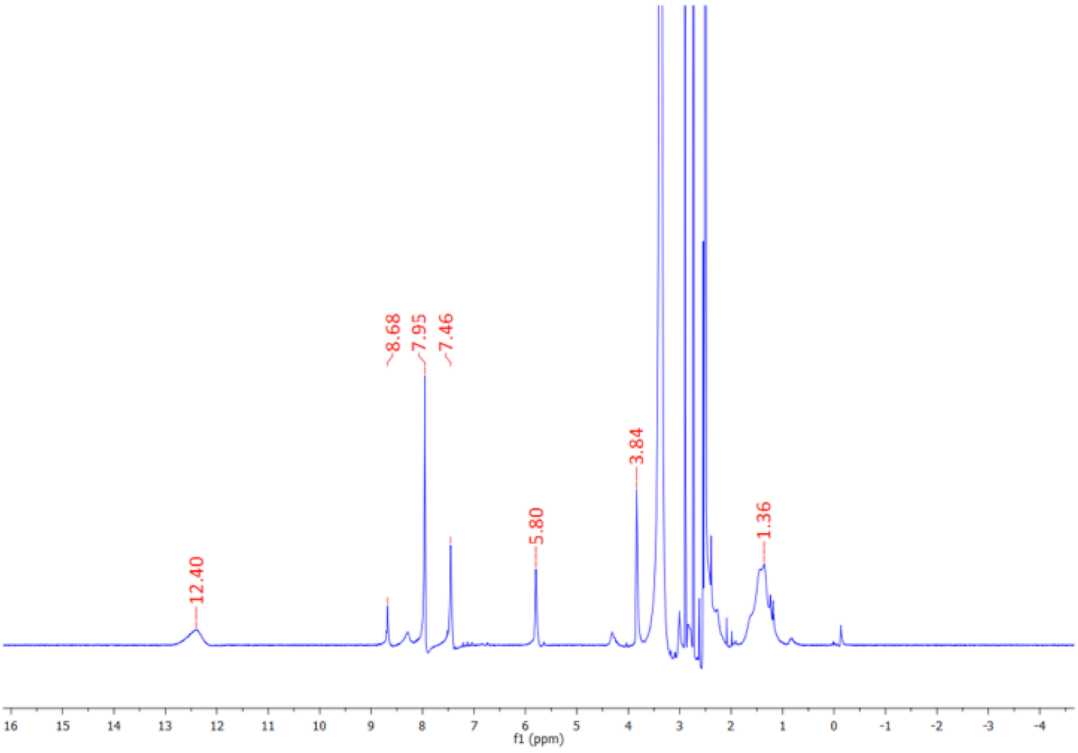


Figure S7 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **P2**.

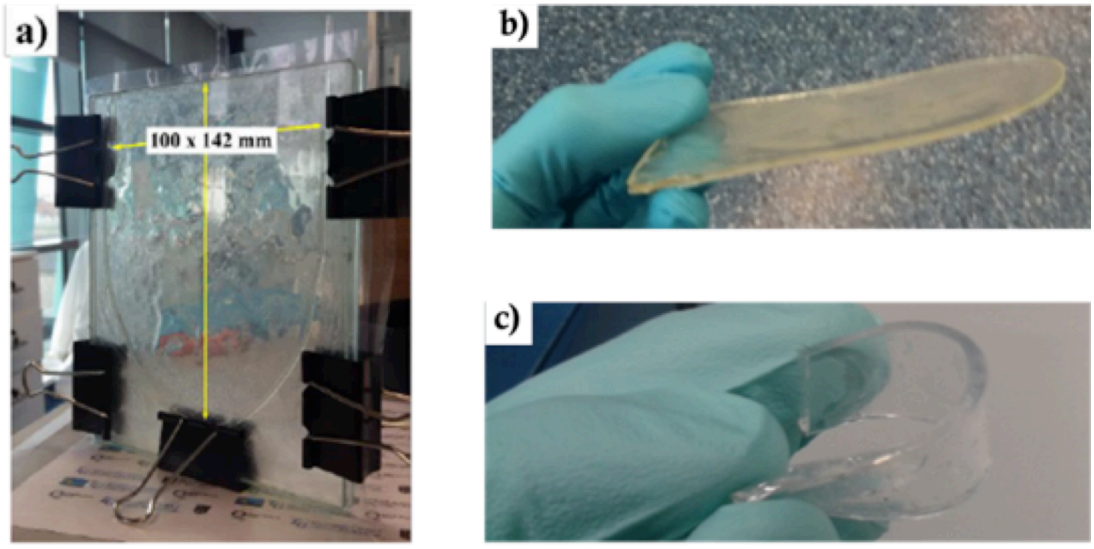


Figure S8 (a) Photograph of cast used to fabricate polymer made from glass and lined with a nono-stick coating (b) Hard and transparent polymer monolith before soaking in solvent (c) Flexible and transparent polymer after soaking in solvent.

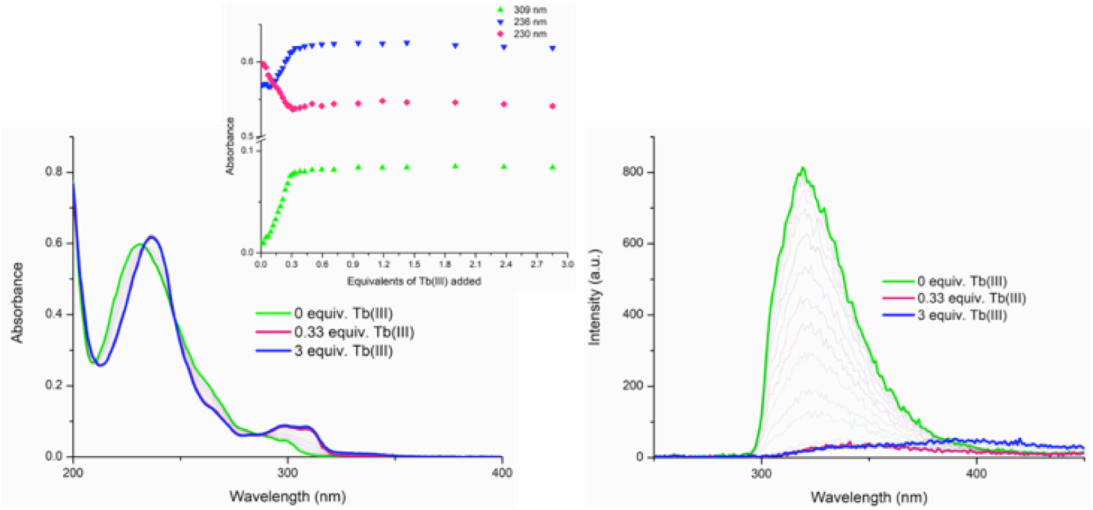


Figure S9 The overall changes in the (left) UV-visible absorption spectra and (right) fluorescence emission spectra (excitation wavelength λ = 237 nm) upon titrating **3** (1×10^{-5} M) against $Tb(CF_3SO_3)_3$ (0→3 equiv.) in CH_3CN at 22˚C. **Inset**: Corresponding experimental binding isotherms of absorbance at λ = 309, 236, and 230 nm.

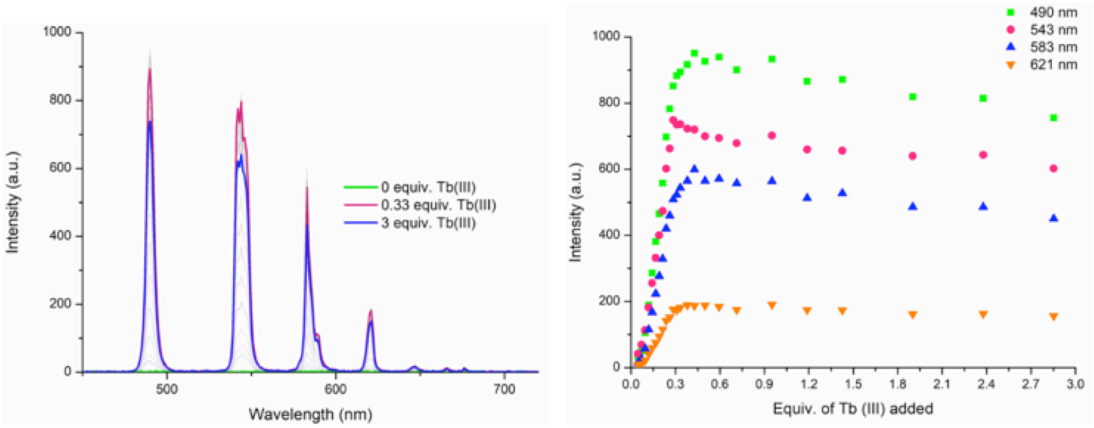


Figure S10 (Left) The overall changes to the Tb(III)-centred phosphorescence spectra upon titrating **3** (1×10^{-5} M) against $Tb(CF_3SO_3)_3$ (0→3 equiv.) in CH_3CN at 22˚C. (right) corresponding experimental binding isotherms of phosphorescence at λ = 490, 545, 583 and 621 nm.

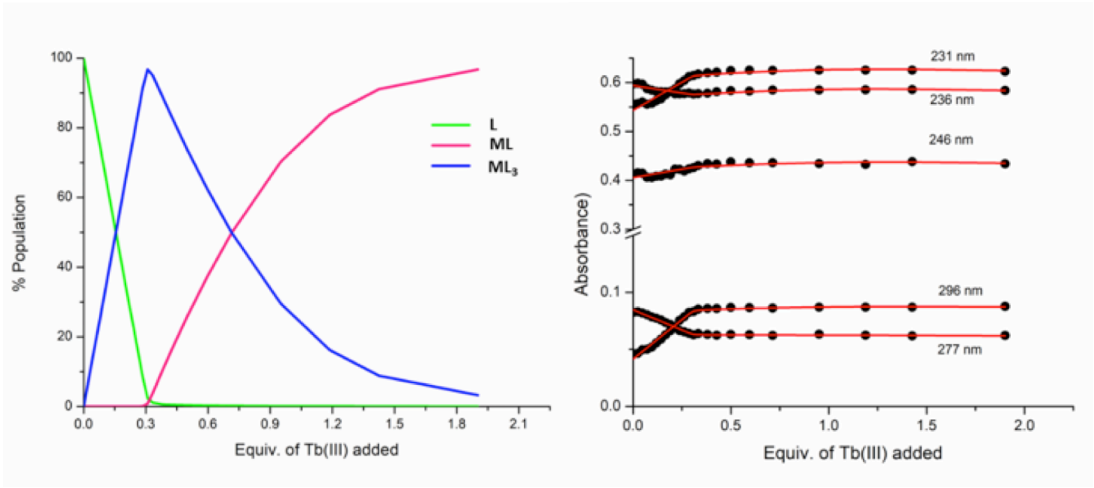


Figure S11 (Left) The speciation distribution diagram obtained from the fit of the UV-visible absorption titration data of ligand **3** against $Tb(CF_3SO_3)_3$ in CH_3CN. (Right) The fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.

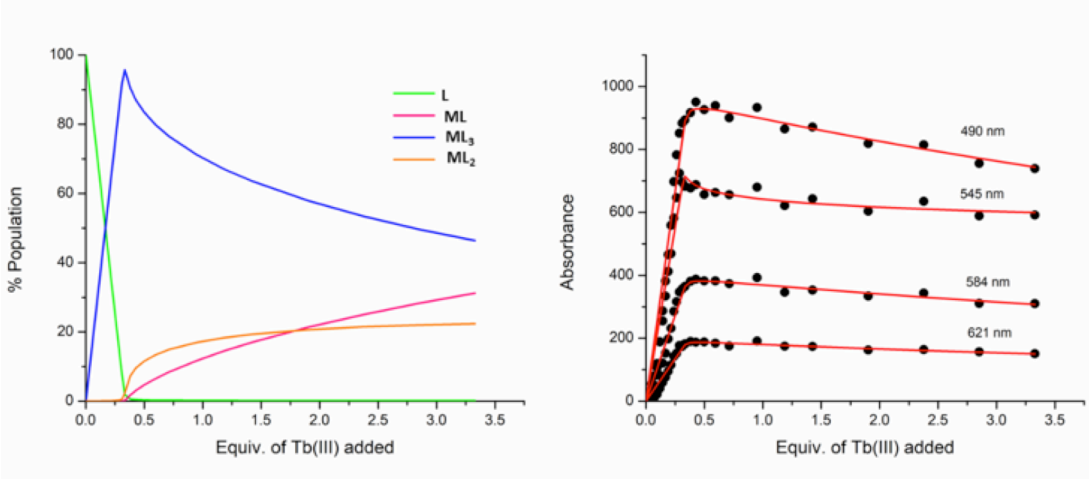


Figure S12 (left) The speciation distribution diagram obtained from the fit of the Tb-centred phosphorescence titration data of ligand **3** against $Tb(CF_3SO_3)_3$ in CH_3CN. (right) the fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.

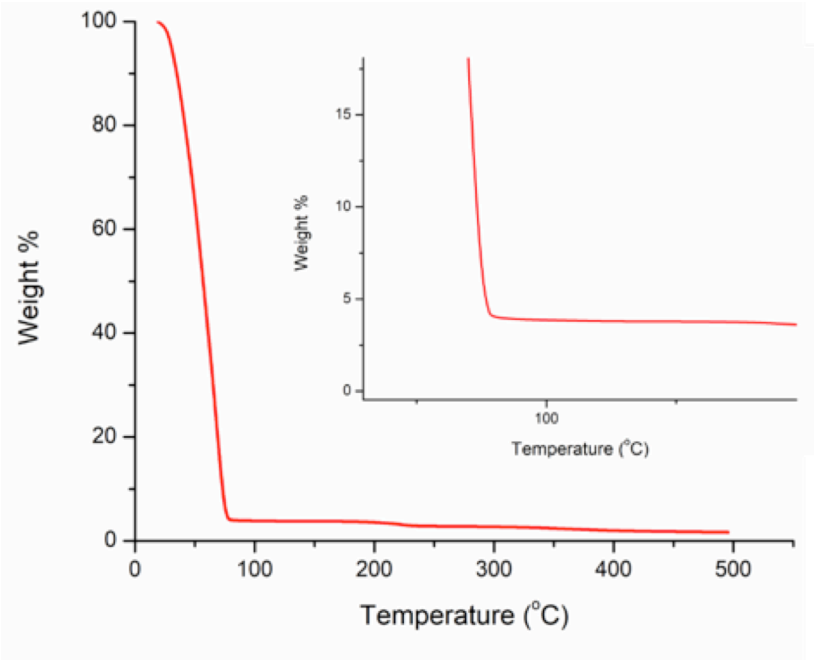


Figure S13 *TGA thermograph of **1** gel showing weight loss of 96.2% before 100 ˚C.*

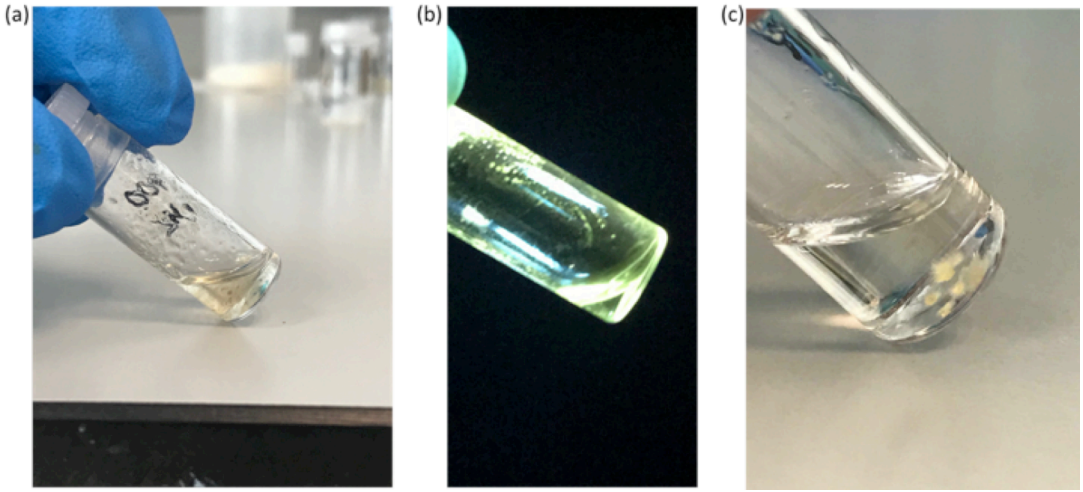


Figure S14 (a) Image of the gel which solubilised upon addition of $Tb(CF_3SO_3)_3$ (b) green emission from the solution following addition of $Tb(CF_3SO_3)_3$ to **1** gel under UV-irradiation (λ_{ex} = 254 nm) (c) crystals of **1** formed from low wt% gel overnight.

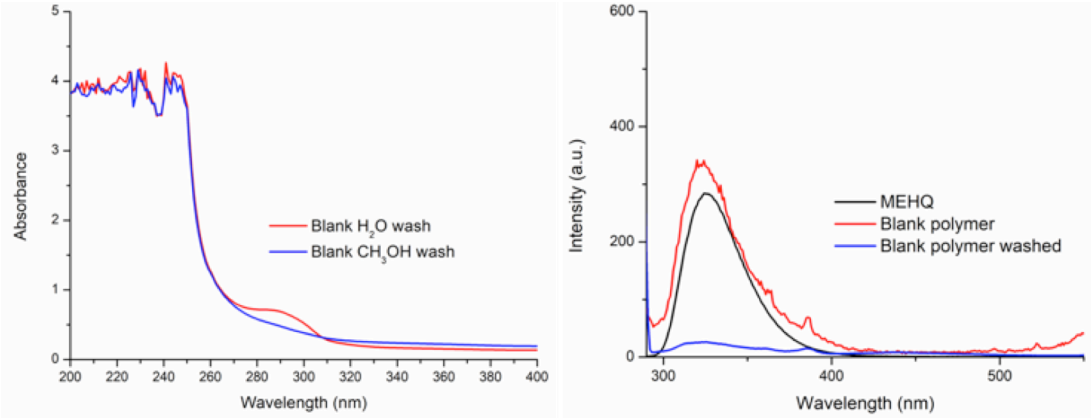


Figure S15 (Left) UV-visible absorption spectrum of blank polymer before and after CH_3OH soak measured in H_2O (right) fluorescence spectrum of MEHQ, blank polymer before and after CH_3OH soak measured in H_2O.

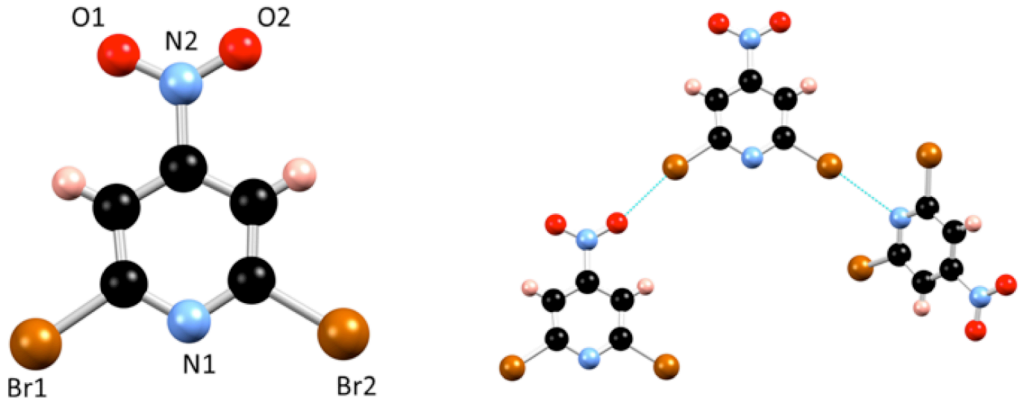


Figure S16 (Left) Structure of one unique molecule of compound **6** with heteroatom labelling scheme, (right) primary mode of interaction between molecules of **6**.

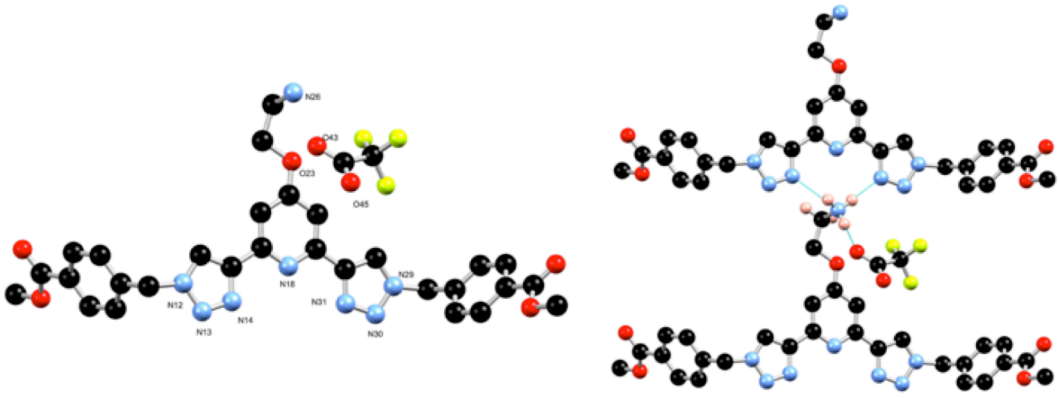


Figure S17 (Left) Structure of one unique molecule of compound **1** with heteroatom labelling scheme and all hydrogen atoms omitted for clarity. (Right) Hydrogen bonding interaction between molecules. Selected hydrogen atoms omitted for clarity.

Table S1 Crystal and refinement parameters for structures **6** and **1**

Identification code	**6**	**1**
Empirical formula	$C_5H_2Br_2N_2O_2$	$C_{33}H_{32}F_3N_9O_7$
Formula weight	281.91	723.67
Temperature/K	100(2)	99.98
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	C2/c
a/Å	5.3120(2)	37.042(7)
b/Å	7.5807(2)	9.974(2)
c/Å	19.3315(6)	18.080(4)
α/°	90	90
β/°	90	96.40(3)
γ/°	90	90
Volume/Å^3	778.45(4)	6638(2)
Z	4	8
ρ_{calc}g/cm^3	2.405	1.448
μ/mm^{-1}	10.361	0.984
F(000)	528.0	3008.0
Crystal size/mm^3	0.14 × 0.05 × 0.04	0.29 × 0.19 × 0.05
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.214 to 66.536	4.8 to 117.862
Index ranges	-7 ≤ h ≤ 8, -11 ≤ k ≤ 11, -29 ≤ l ≤ 29	-40 ≤ h ≤ 39, -11 ≤ k ≤ 11, -15 ≤ l ≤ 19
Reflections collected	18543	13925
Independent reflections	2983 [R_{int} = 0.0441, R_{sigma} = 0.0347]	4650 [R_{int} = 0.0780, R_{sigma} = 0.0881]
Data/restraints/parameters	2983/0/100	4650/0/473
Goodness-of-fit on F^2	1.072	0.965
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0680	R_1 = 0.0703, wR_2 = 0.1784
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.0707	R_1 = 0.1271, wR_2 = 0.2143
Largest diff. peak/hole / e Å^{-3}	0.99/-0.96	0.29/-0.30
Flack parameter	0.040(7)	

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