NIR emitting Ytterbium chelates for colourless luminescent solar concentrators.

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Supporting Information

1. **Synthesis of the ytterbium chelate and preparation of the PMMA slab**
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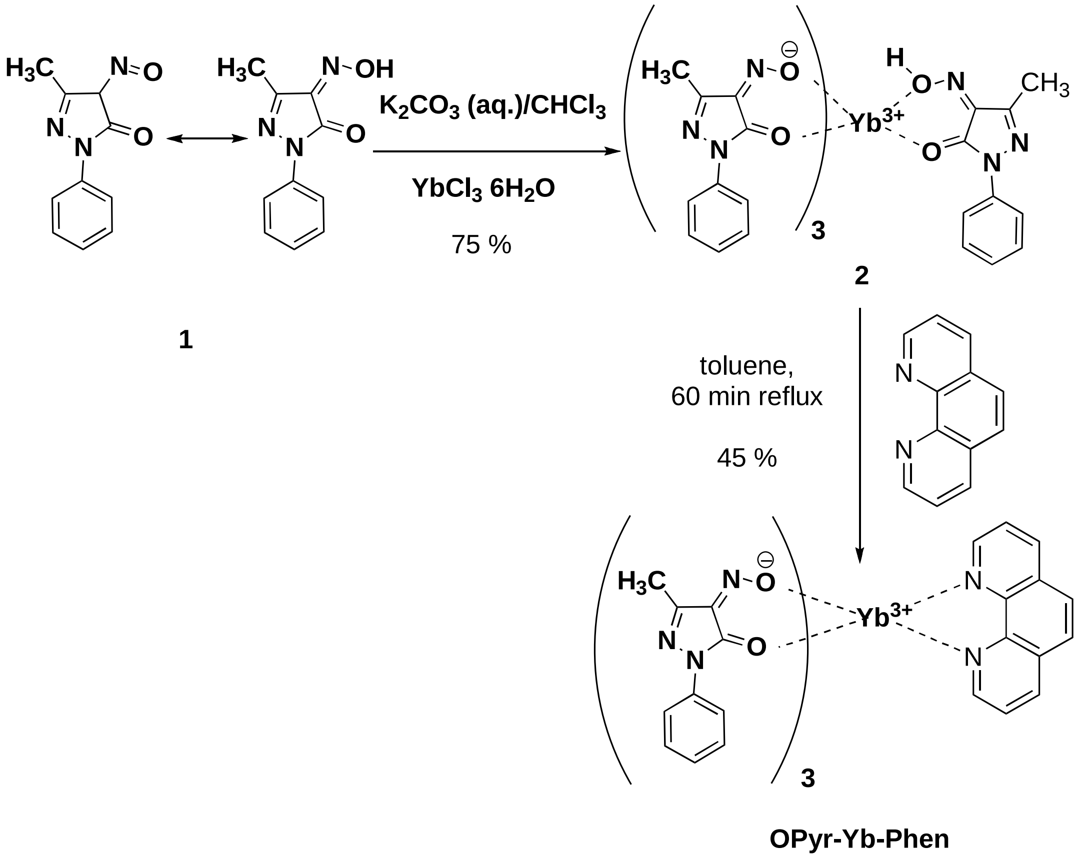
9. **0.1 % (by weight) OPyr-Yb-Phen containing PMMA slab luminescence decay at 1010 nm.**

1. Synthesis of the ytterbium chelate.

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 and 125.70 MHz, respectively. Coupling constants are presented in Hz. Absorption spectrometry was performed using a Jasco V570 spectrophotometer. FT-IR spectra were recorded on a Perkin Elmer 100-TF Infrared operating in Universal ATR configuration. Ytterbium chloride hexa-hydrate was purchased form Alfa-Aesar, all other commercially available chemicals and solvents were purchased from Sigma Aldrich ad used without further purification. Dry solvents were dried overnight over Na_2SO_4 and filtered immediately before use.

The Chelate **OPyr-Yb-Phen** was prepared according to the two-step procedure shown in scheme 1.



Scheme 1.

Tetrakis chelate 2. (Z)-4-(hydroxyimino)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (1.63 g, 8.03 mmol) and K_2CO_3 (1.12 g, 8.10 mmol) were dissolved in 140 ml of distilled water. CHCl3 (80 ml) was added to give a biphasic mixture that was vigorously stirred. A solution of $YbCl_3 * 6H_2O$ in distilled water (20 ml) was added to give a thick yellow suspension. Mixture was stirred overnight, diluted with 50 ml of $CHCl_3$ and separated. Organic phase was dried over Na_2SO_4 and evaporated to give the tetrakis chelate **2** as a yellow solid (1.554 g, 1.58 mmol). This starting material was employed directly in the next step without any further purification.

IR

Figure S1. FT-ATR spectrum of derivative 2.

OPyr-Yb-Phen. The tetrakis chelate **2** (0.502 g, 0.51 mmol) and 1,10-phenanthroline (0.095 mg, 0.53 mmol) were refluxed in toluene (40 ml) for 1 h under a Dean-Stark trap. The clear yellow solution was left to stand overnight at room temperature. The chelate slowly precipitates as yellow needles that were recovered by suction filtration (0.221 g, 0.23 mmol, yeld 45.1 %). Anal Calcd for $C_{42}H_{32}N_{11}O_6Yb$: C, 52.56; H, 3.36; N, 16.05; Calcd For $C_{42}H_{32}N_{11}O_6Yb * 3/2\ H_2O$: C, 51.59; H, 3.50; N, 15.76. Found: C, 52.02; H, 3.45; N, 15.28.

Preparation of the PMMA slab. In a typical procedure for the preparation of a 0.1 % slab, 100 mg of AIBN were dissolved in 100 ml of freshly distilled MMA. The solution was placed in a beaker and slowly heated on a hot plate until the temperature of 80 °C was reached. This temperature was maintained for 2 minutes, during which time viscosity increased substantially. The solution was immediately transferred in an ice bath and cooled at 20°C. A solution of **OPyr-Yb-Phen** (160 mg) in freshly distilled MMA (60 ml) was added along with 150 mg of lauryl peroxide. The viscous syrup thus obtained was poured in a mould of 7 mm thickens and 100 cm2 area and heated in a water bath at 56°C for 48 h. At the end of this thermal treatment the syrup turns into a solid slab that is further cured at 95°C for 24 h. After cooling, the slab can be easily separated by the glass mould, cutted and polished for optical measurements.

Figure S2 shows the typical setup we employed for the preparation of the slabs.

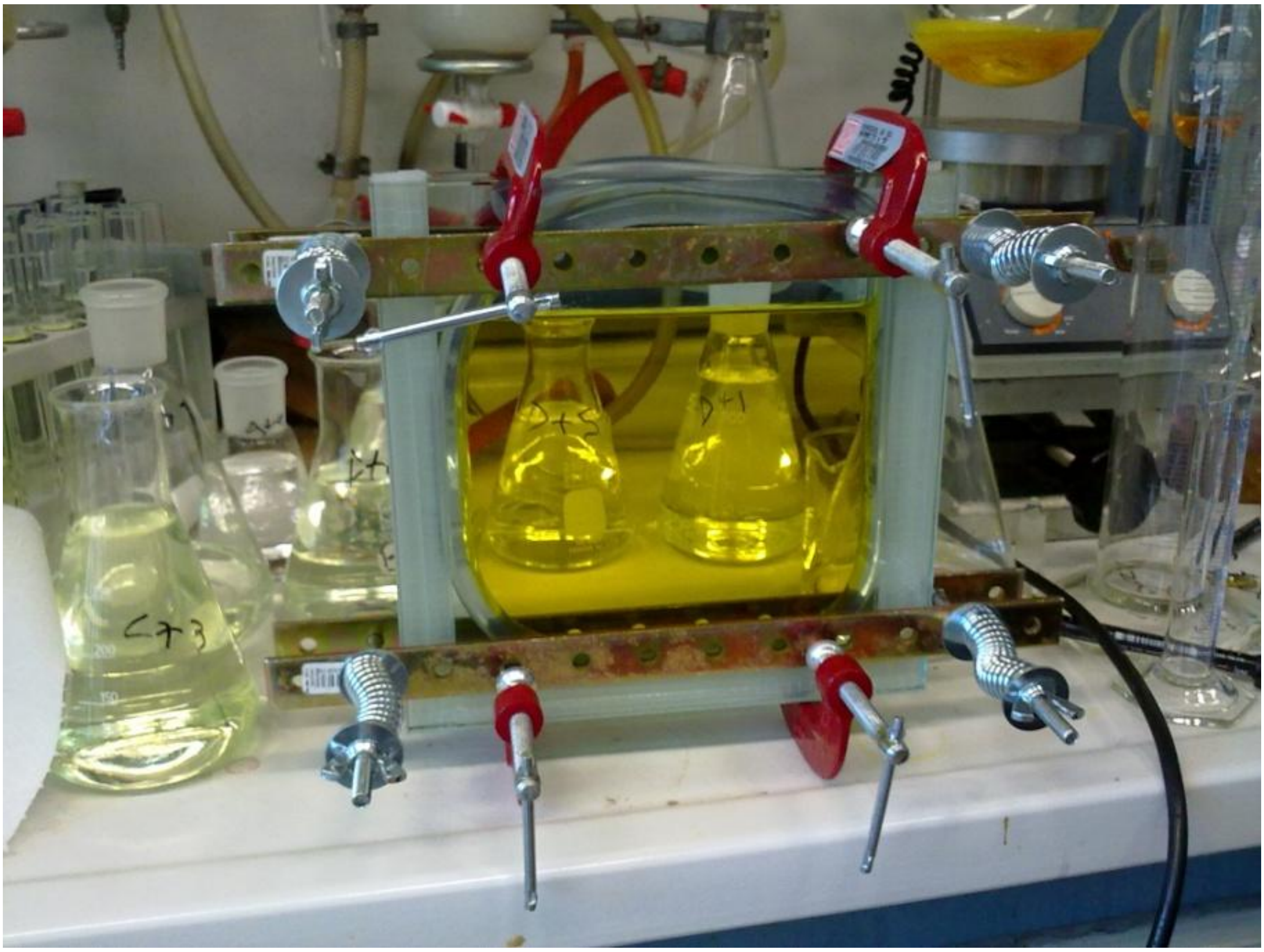
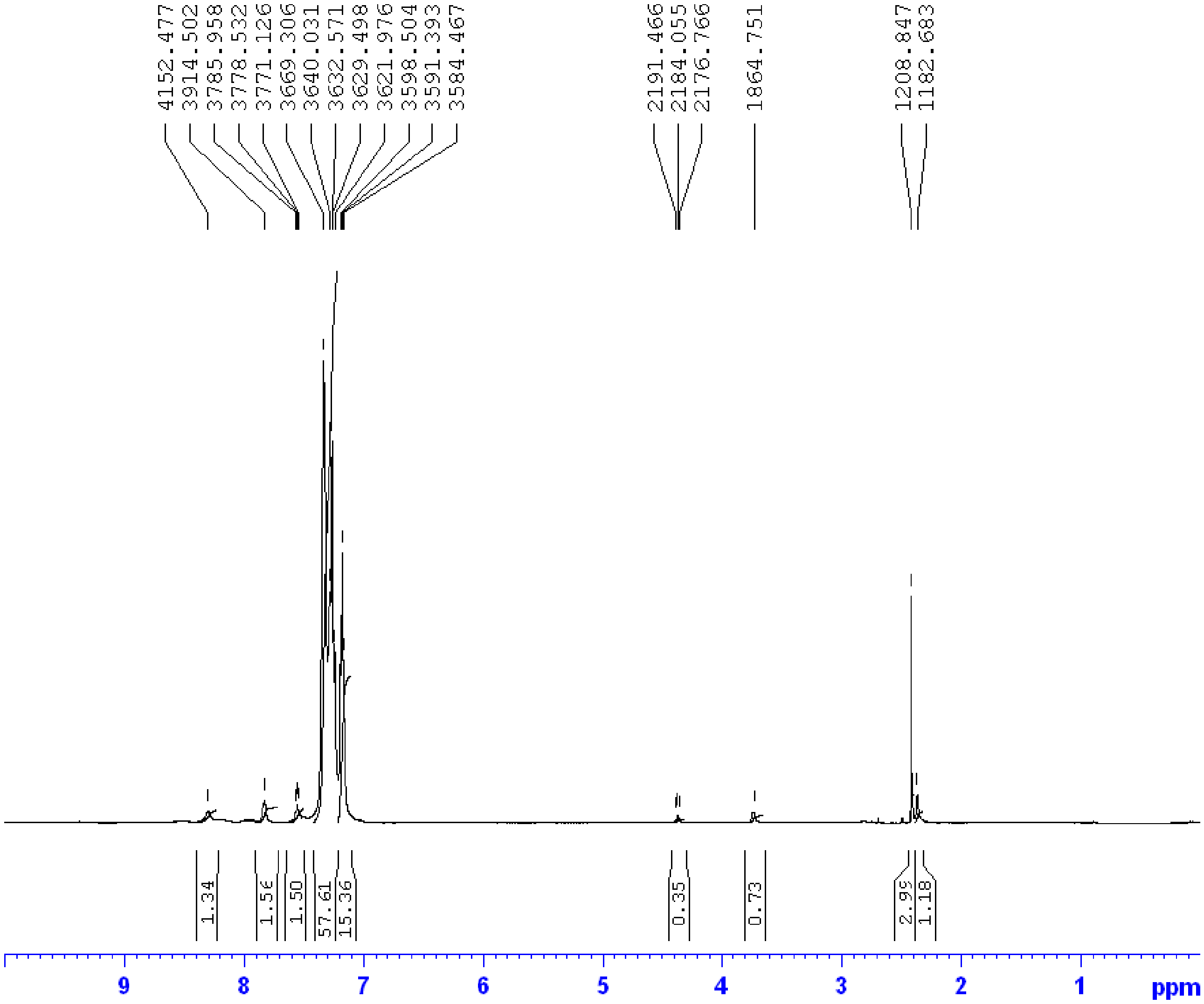
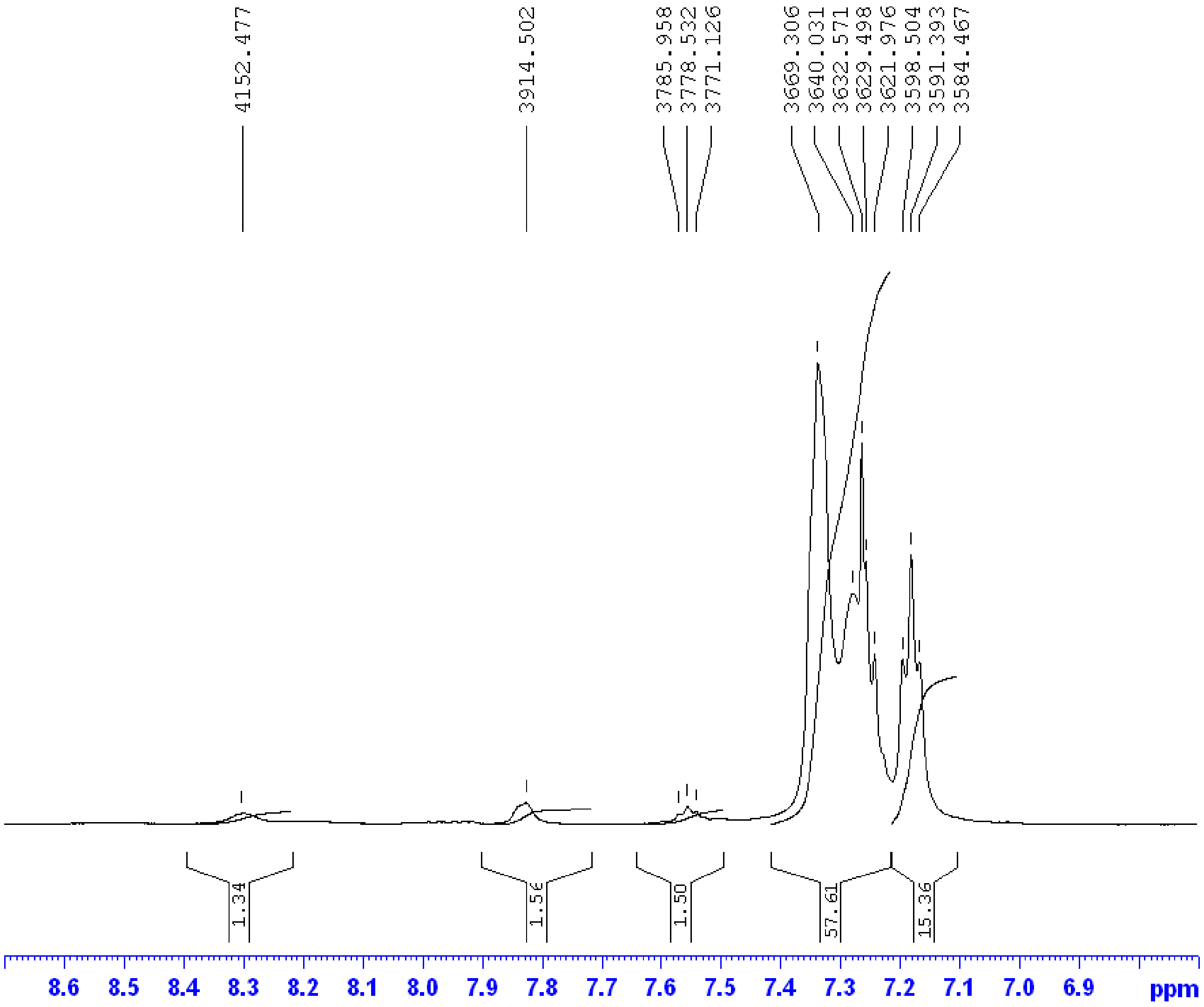


Figure S2. Experimental set-up for slabs preparation.

2. ^{1}H NMR spectrum of OPyr-Yb-Phen

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1.56
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8.5
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8.3
8.2
8.1
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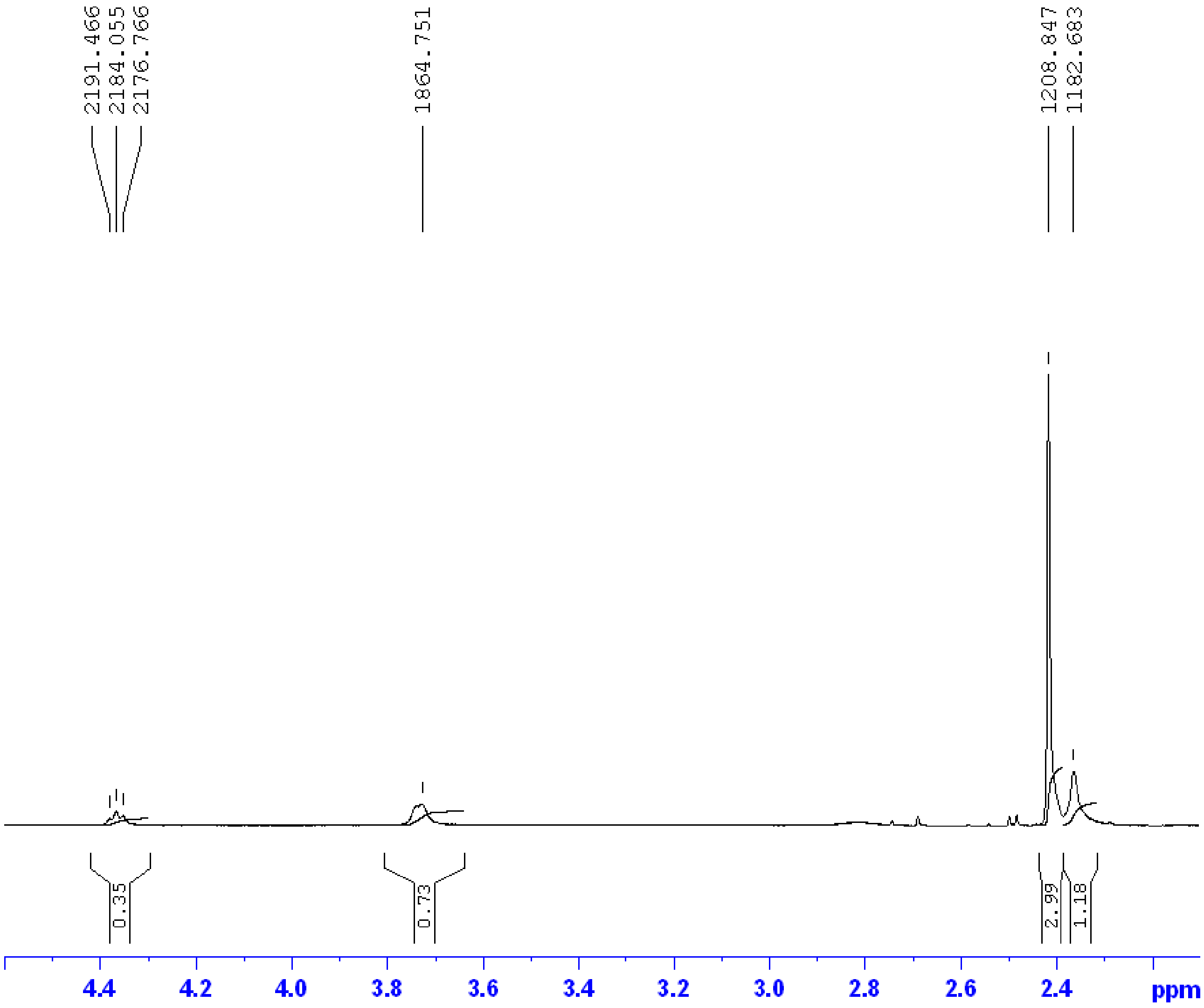
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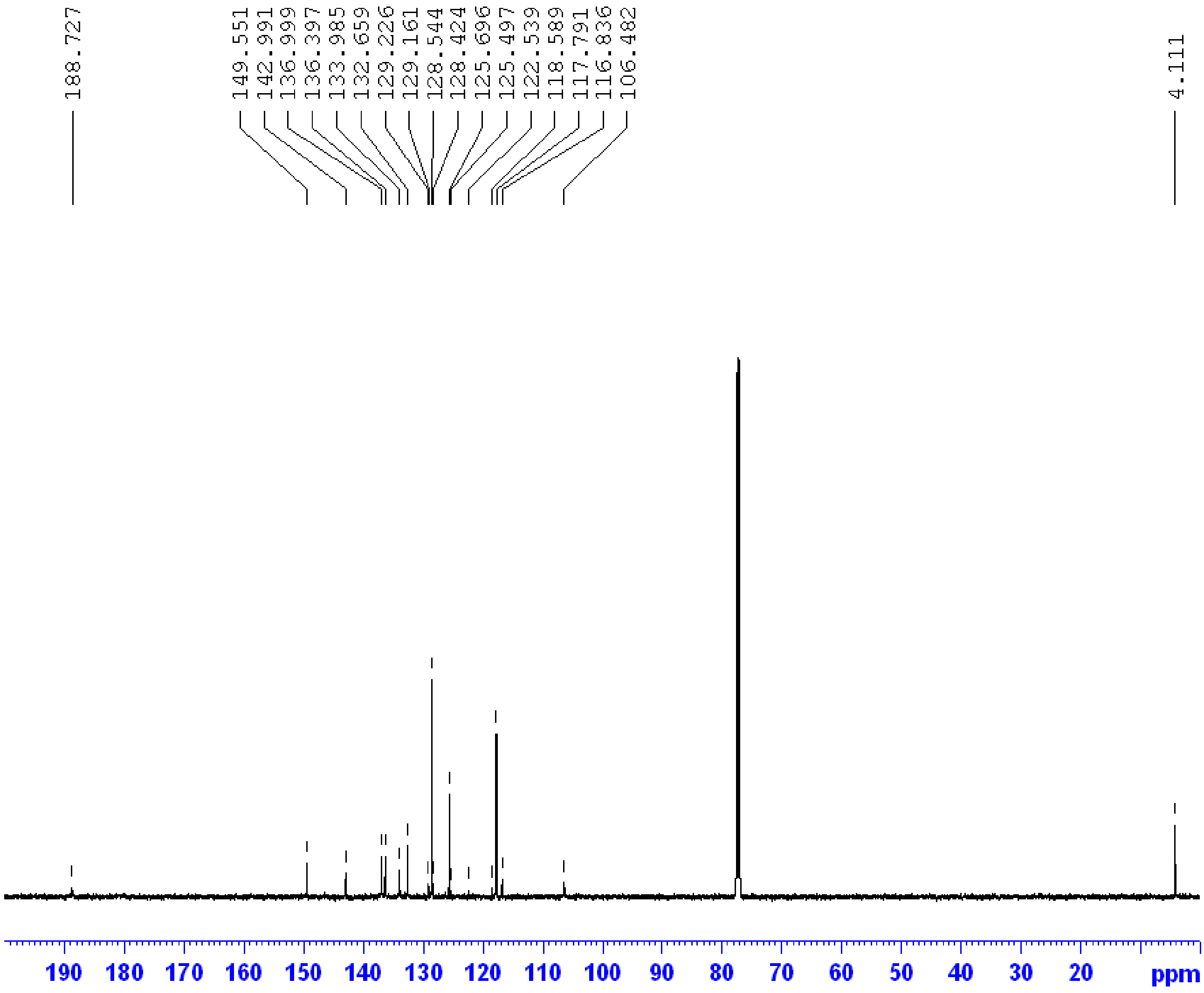
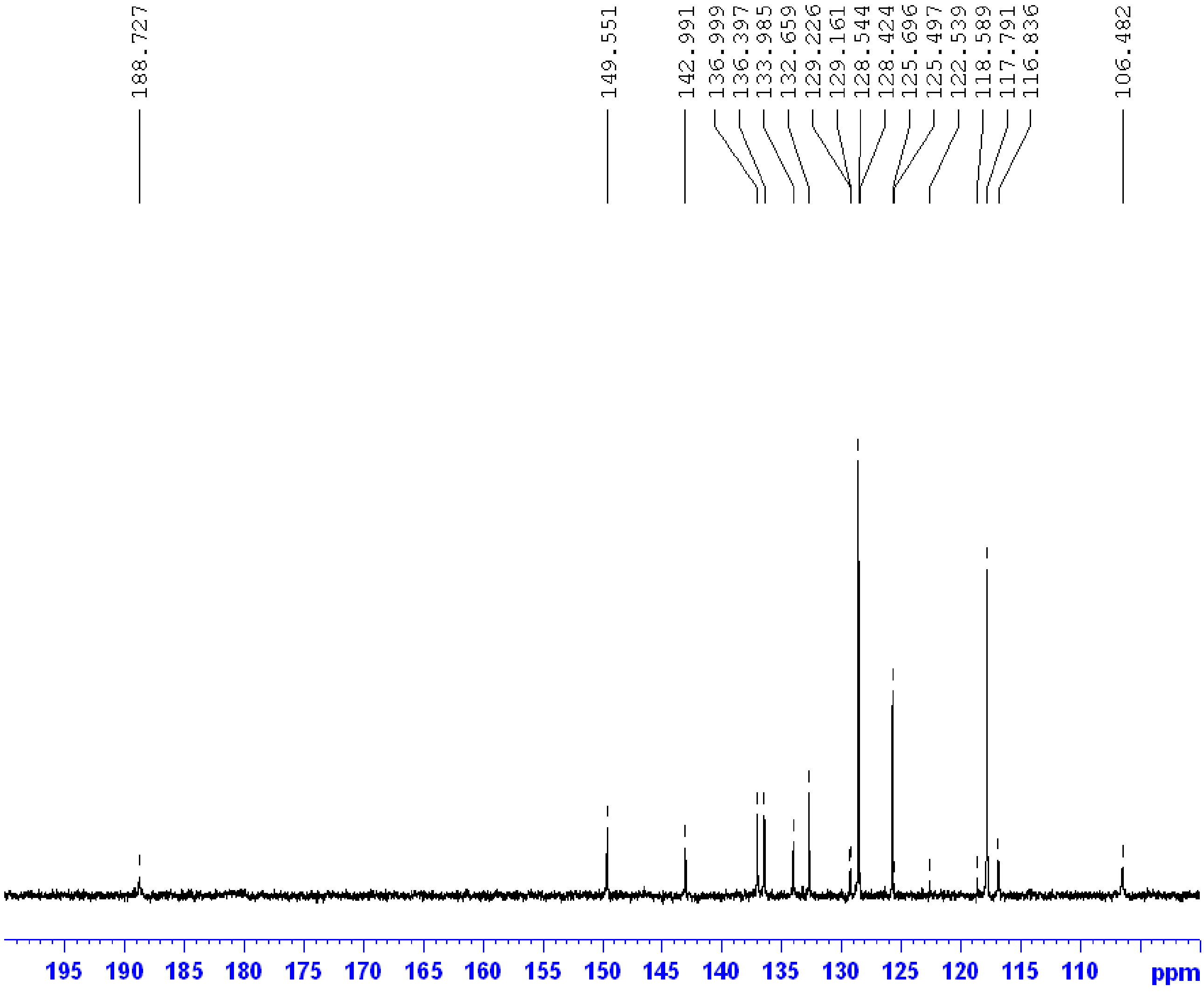
2.6
2.4
ppm

3. ^{13}C NMR spectrum of OPyr-Yb-Phen.

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117.791
116.836
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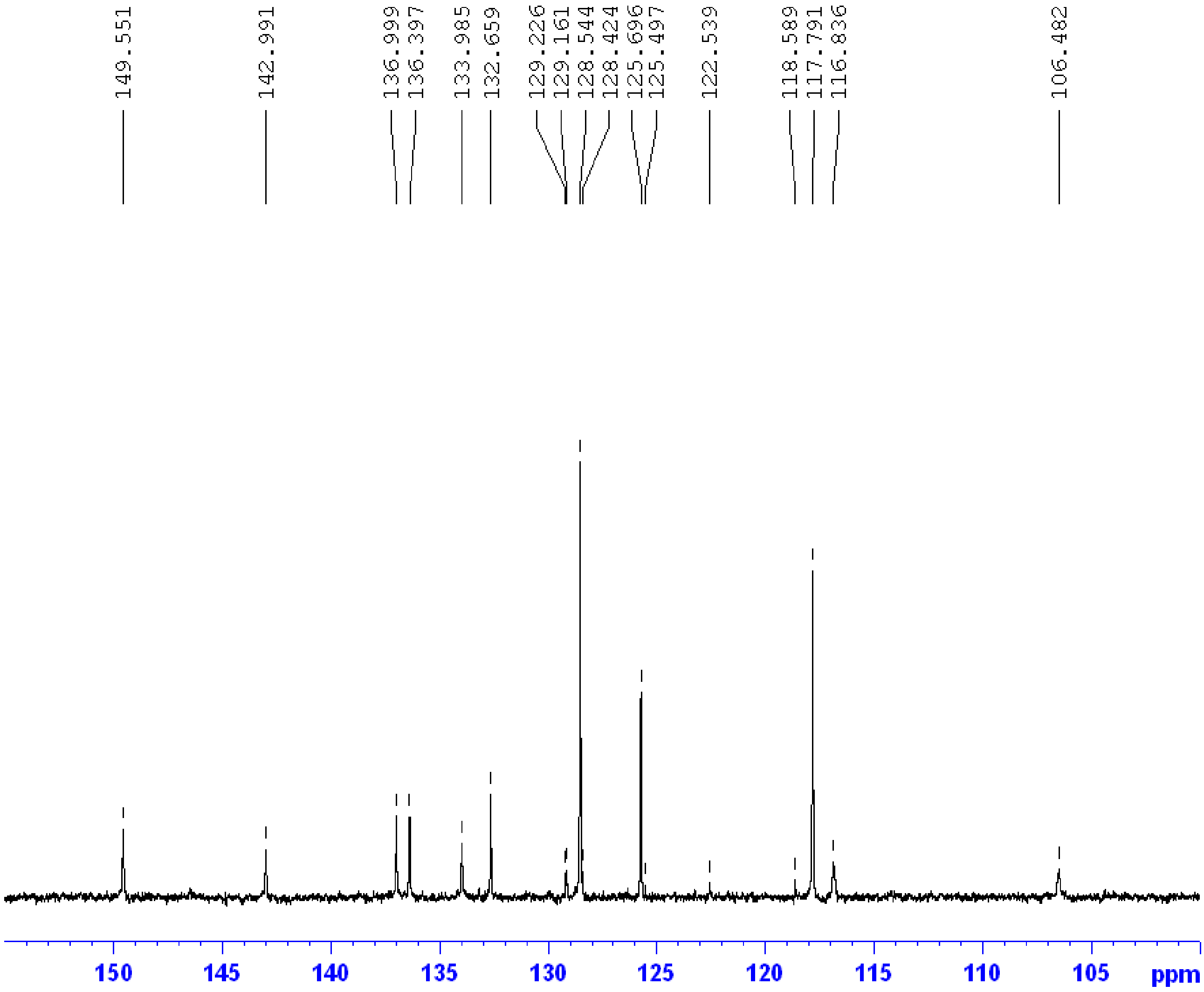
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122.539
118.589
117.791
116.836
106.482
150
145
140
135
130
125
120
115
110
105
ppm

4. Figure S3. FT-IR spectrum of OPyr-Yb-Phen.

The spectrum was recorded in ATR configuration directly on the chelate powder.

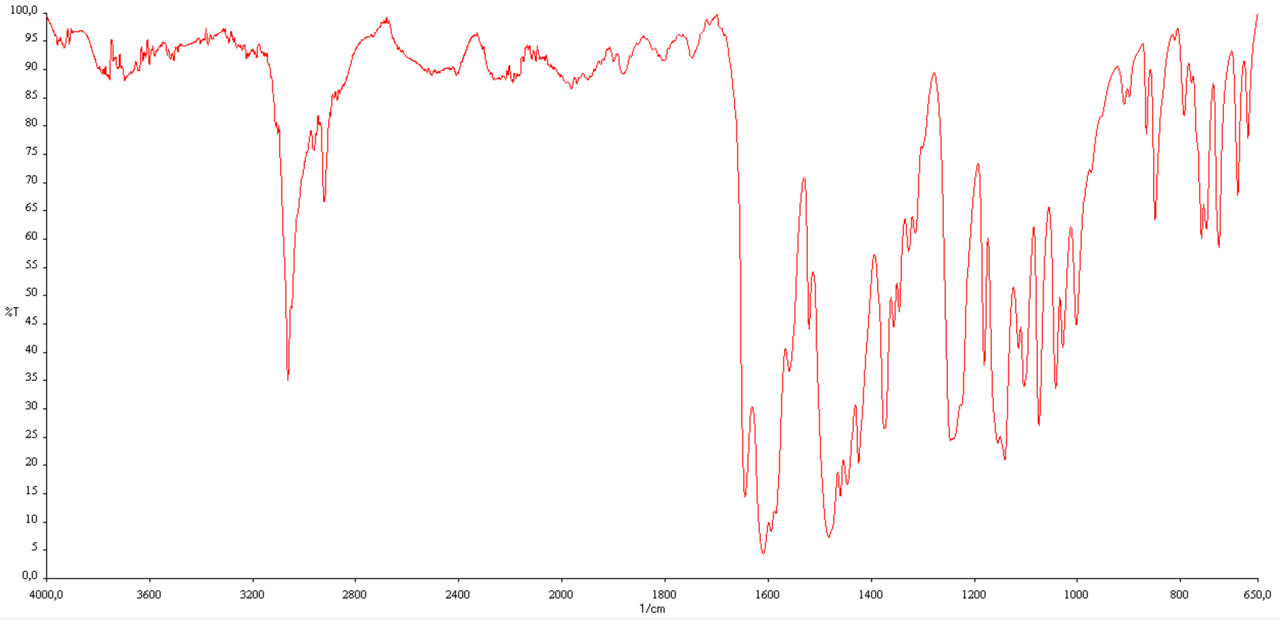


Figure S3. FT-ATR spectrum of chelate OPyr-Yb-Phen.

5. X-Ray crystallographic information.

Crystal Structure Determinations: Compound **OPyr-Yb-Phen** has been crystallized from toluene by isothermal solvent evaporation. This procedure gave crystals with and without chlathrated toluene molecules (**OPyr-Yb-Phen(1)** and **OPyr-Yb-Phen(2)**, respectively, in the following). A crystal of either species was mounted on a Rigaku R-Axis II diffractometer and cooled to 130(1) and 110(1) K, respectively, for cell parameters measurement and data collection. Crystals of **OPyr-Yb-Phen(1)** showed small cracks due to slight solvent loss during manipulation but were however of good diffracting quality. The collected intensities were corrected for Lorentz and polarization factors and absorption using CrystalClear-SM Expert 2.0© suite of programs. The structures were solved by direct methods (SIR2008) and refined by full-matrix least-squares on Fo^2 by using anisotropic displacement parameters for all non-H atoms. All the hydrogen atoms including those of the solvent molecules in **OPyr-Yb-Phen(1)**, were located on difference Fourier maps. Hydrogen atoms were included in their calculated positions and refined using SHELXL97 using a riding model with ADPs 1.2 or 1.5 times the ADPs of the parent sp^2 and methyl carbon atoms, respectively. One the toluene molecules (C37-C40) lies disordered on an inversion center and has been properly modeled. All three symmetry independent toluene molecules were refined with DELU command in SHELXL97 for rigid-bond restraints to U_{ij}-values of bonded atoms. Toluene molecule C23-C29 has been constrained with AFIX 66 instruction to a rigid group refinement.

Table S1. Crystal and structure refinement data for **OPyr-Yb-Phen(1)** and **OPyr-Yb-Phen(2)**

Compound	**OPyr-Yb-Phen(1)**	**OPyr-Yb-Phen(2)**
formula	$C_{119}H_{104}N_{22}O_{12}Yb_2$	$C_{42}H_{32}N_{11}O_6Yb$
formula weight	2380.32	959.83
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
Z	1	2
F(000)	1208	958
a (Å)	12.7550(4)	11.1020(3)
b (Å)	13.8809(5)	12.5751(4)
c (Å)	16.4661(6)	16.8441(6)
α (deg)	104.3437(11)	71.390(3)
β (deg)	104.5929(10)	75.122(4)
γ (deg)	99.8816(10)	79.674(5)
volume (Å^3)	2646.82(16)	1948.81(12)
calc density (g cm^{-3})	1.493	1.636
μ (mm^{-1})	1.831	2.464
temperature (K)	130(2)	110(2)
max/min transm factor	0.669, 0.569	0.752, 0.646
θ_{max} (deg)	27.0	27.61
hkl range	-16 to16 -17 to17 -19 to 21	-13 to10 -16 to 16 -21 to 21
no. of measured reflns	29486	36460
no. of unique reflns, R_{int}	11252 (0.0425)	8919 (0.0503)
no. of obsd reflns ($I > 2\sigma(I)$)	10846	8682
parameters	685	544
constraints/restraints	36	
completeness to θ, %	97.4	98.6
absorption correction	numerical	numerical
GOF (all)	1.092	1.122
R_1 ($I > 2\sigma(I)$)	0.0299	0.0284
R_1 (all data)	0.0317	0.0297
wR_2 (all)	0.0668	0.0634
$\Delta\rho$ max,min (e Å^{-3})	0.674, -0.878	1.347, -0.879

$R_{int} = \Sigma \mid F_o^2 - F_o^2(\mathrm{mean}) \mid / \Sigma [F_o^2]$ $R_1 = \Sigma \mid |F_o| - |(1/k)F_c| \mid / \Sigma |F_o|$

$wR_2 = [\Sigma w(F_o{}^2 - (1/k)F_c^2)^2 / \Sigma w|F_o^2|^2]^{1/2}$, GOF $= [\Sigma w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$

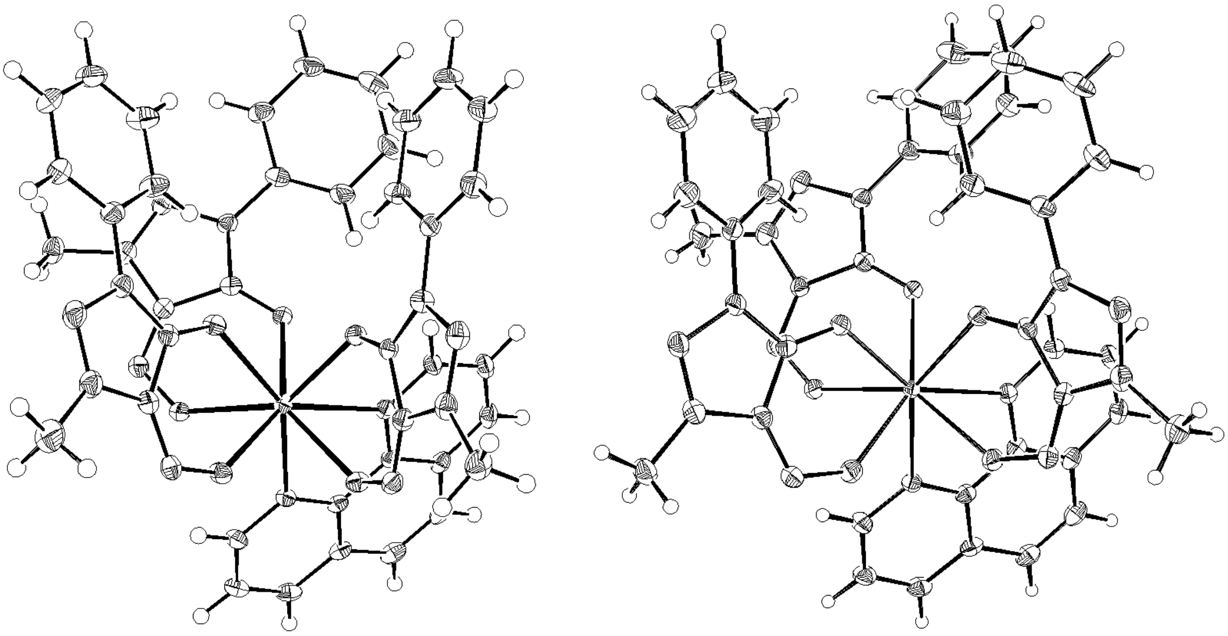


Figure S4. Molecular structures for **OPyr-Yb-Phen(1)** (left) and **OPyr-Yb-Phen(2)** (right). Ellipsoids were drawn at 40% probability level. Hydrogen atoms were given with arbitrary radii.

The CIF file containing the complete information is included as a separate file.

6. Details on computational results.

6.1 Computational methods

Ab initio calculations on **OPyr-Yb-Phen** use the quasi-relativistic effective core potential (ECP) of Dolg *et al*[1] and the related [5s4p3d]-GTO valence basis sets for the yetterbium ion. This ECP includes $46+4f^{n}$ electrons in the core, leaving the outermost 11 electrons to be treated explicitly. Preliminary investigation of several geometrical arrangements of ligand **1** and phenantroline around the ytterbium ion was performed at the Hartree-Fock level, using the 3-21G basis set for the ligand atoms. The obtained structures were successively refined by optimization at the Density Functional Theory level, with the hybrid PBE1PBE functional [2] and the 6-311G** basis sets for the ligand atoms. Stationary points were characterized by frequency calculations. All calculations were performed with the Gaussian 09 program [3].

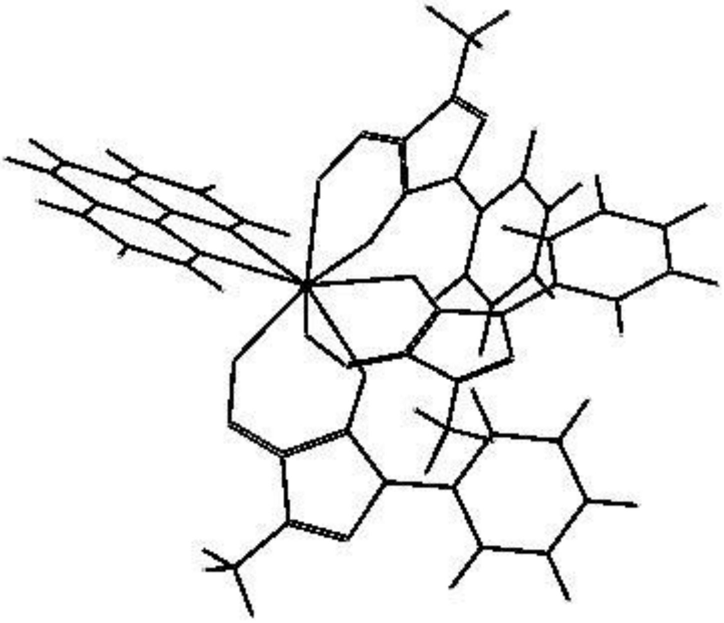
Amongst all the obtained isomers, two (labeled as C_1 and C_2) are more stable than the other and almost isoenergetic (ΔE = 0.05 kcal mol^{-1}). Moreover, the C_2 isomer matches the X-ray structure.

[1] Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta*. **1989**, *75*, 173-194.

[2] Adamo, C.; Barone, V. *J. Chem. Phys.* **2002,** *116*, 5933-5940.

[3] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JrJA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.02. Gaussian Inc. Wallingford CT.

6.2 Electronic energy (Hartree) and atomic coordinates of the C_1 isomer of **OPyr-Yb-Phen** calculated at the PBE1PBE/6-311G** level



Energy (Hartree) -2710.48777583

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6	0.764738	3.360923	-1.464259
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6	3.905096	3.173798	0.314707
6	1.009235	5.708012	-2.597080
7	-0.422582	3.029978	-1.928991
8	1.455332	1.484674	-0.076711
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6	6.105434	3.897991	0.961877

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1	0.829445	5.363749	-3.619182
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6	5.239816	1.819488	1.785156
6	4.055733	2.020413	1.088243
1	4.793961	5.003796	-0.347081
1	6.899296	4.635848	0.908745
1	7.190165	2.583003	2.276161
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6	-2.270731	0.681646	5.517117
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8	-2.242739	0.701537	0.578908
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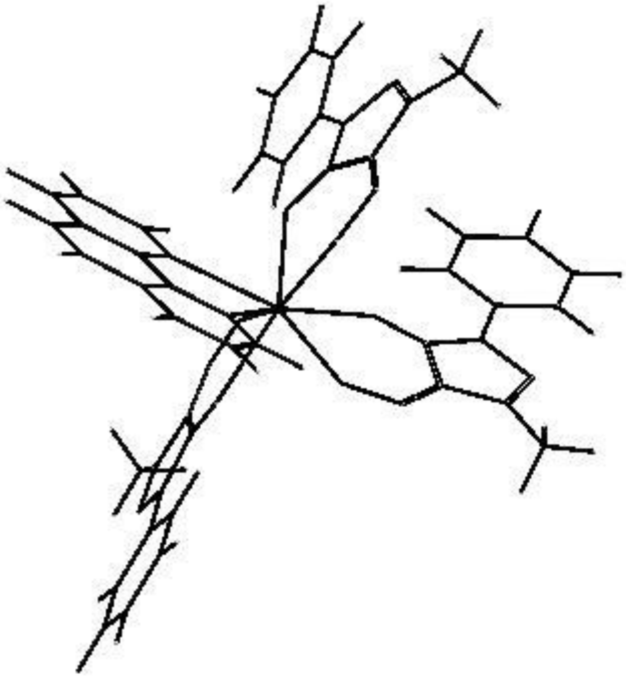
1	5.369327	-3.889276	4.255195
1	3.403341	-2.378313	4.115275
1	2.613116	-1.552315	1.936314
70	-0.263997	-0.008443	-0.400842

6.3 Electronic energy (Hartree) and atomic coordinates of the C_2 isomer of **OPyr-Yb-Phen** calculated at the PBE1PBE/6-311G** level



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6	1.514445	3.570201	-2.181852
6	2.471042	2.746375	-1.586778
1	2.252897	1.701934	-1.409969
6	3.703475	3.281305	-1.234233
1	4.445478	2.633031	-0.780071
6	3.992977	4.619945	-1.470114
1	4.960604	5.026666	-1.196602
6	3.035315	5.429139	-2.071411
1	3.251337	6.473874	-2.269531

6	1.798351	4.913438	-2.428291
1	1.049236	5.526074	-2.912658
8	0.235191	0.165045	1.441029
8	-0.929228	-2.418973	1.254453
7	1.576787	0.050008	3.341882
7	1.895184	-0.877811	4.328435
7	-0.301051	-2.732419	2.312960
6	0.716596	-0.454657	2.413231
6	0.486950	-1.815177	2.842313
6	1.263919	-1.973936	4.041606
6	1.383556	-3.193362	4.877691
1	2.021955	-2.990203	5.737949
1	1.811195	-4.015499	4.297291
1	0.399199	-3.521785	5.221805
6	2.123168	1.347305	3.427253
6	2.157714	2.189242	2.313446
1	1.762724	1.852968	1.364520
6	2.708254	3.458961	2.435351
1	2.739972	4.100128	1.560347
6	3.226391	3.896652	3.647927
1	3.657185	4.888472	3.733377
6	3.196481	3.046857	4.747909
1	3.604520	3.372414	5.699226
6	2.648600	1.776906	4.646240
1	2.629874	1.100387	5.490456
8	1.170996	-1.434658	-0.756455
8	-1.242078	-2.568856	-1.671513
7	2.829270	-2.882234	-1.527421
7	2.904858	-4.058747	-2.268352
7	-0.558668	-3.509497	-2.190770
6	1.545313	-2.459439	-1.364982
6	0.749229	-3.451933	-2.051151
6	1.693377	-4.401039	-2.576597

6	1.395277	-5.620384	-3.366581
1	2.323662	-6.133547	-3.618629
1	0.861589	-5.361774	-4.285165
1	0.749390	-6.296035	-2.799284
6	4.026445	-2.295200	-1.064143
6	4.006741	-1.216644	-0.176508
1	3.062921	-0.812974	0.159784
6	5.207062	-0.673406	0.262879
1	5.180809	0.157480	0.960701
6	6.423461	-1.186151	-0.169237
1	7.355698	-0.756533	0.181080
6	6.431868	-2.260084	-1.051560
1	7.373562	-2.673667	-1.397262
6	5.244540	-2.817933	-1.500929
1	5.238357	-3.658294	-2.181700

7. General details on photophysical characterizations.

Photoluminescence Studies: For VIS and NIR PL measurements, the compounds were excited by a 355 nm (3.49 eV) Nd:YAG laser (Laser Export mod. LCS-DTL-374QT) with average excitation power of 0.95 mW and a pulse repetition rate of 500 Hz. VIS (NIR) luminescence has been detected by a PMT Hamamatsu R943-02 (Hamamatsu R5509-73) coupled with an high speed amplifier (Hamamatsu C5594) and a 74100 Cornestone 2601/4 (ORIEL) monochromator. The bandwidth used is 3 nm for powder samples. For TRPL measurements, a PCI plug-in multichannel scaler ORTEC 9353 was used in photon counting acquisition mode, with an overall time resolution better than 10 ns. All measurements have been done at room temperature (RT), and have been corrected for the instrumental spectral response. None of the investigated samples showed any photo-induced degradation at the excitation power investigated.

8. OPyr-Yb-Phen CCl_4 solution luminescence decay at 1010 nm as a function of the concentration.

We carried out a study of the PL decay for the Yb^{3+} ion emission at 1010 nm as a function of the concentration in CCl_4 as the solvent. The data of figure S5 clearly show that the presence of the two components of the emission decay are not related to aggregation phenomena.

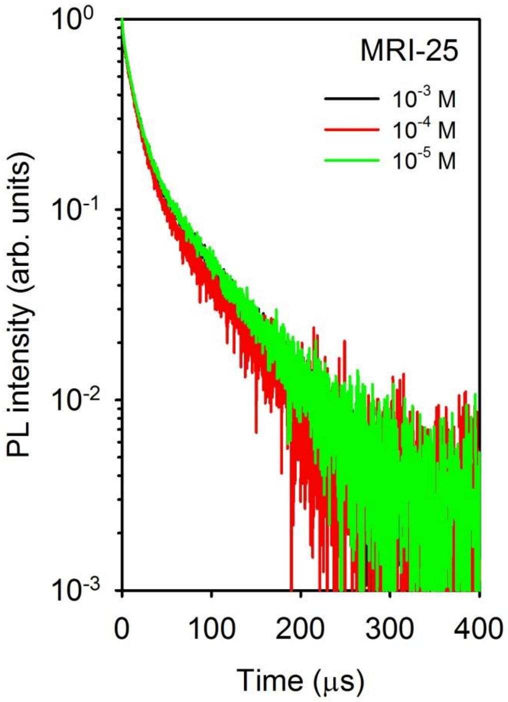

Figure S5. PL decay of **OPyr-Yb-Phen** solution at 1010 nm as function of the concentration under pulsed excitation at 355 nm (500 Hz, average power 0.95 mW)

9. 0.1 % (by weight) OPyr-Yb-Phen containing PMMA slab luminescence decay at 1010 nm.

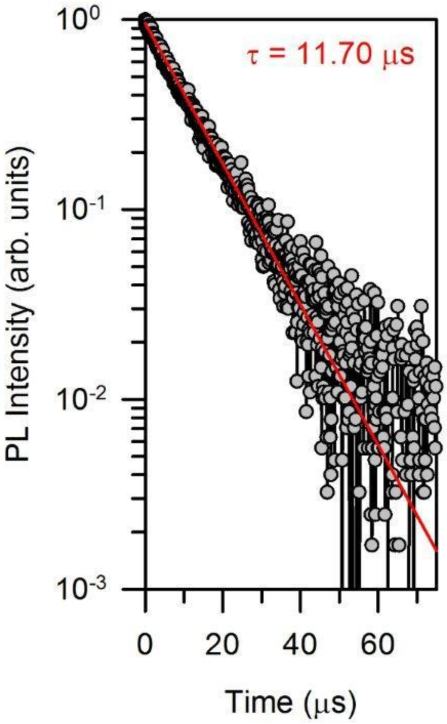

Figure S6. **OPyr-Yb-Phen** containing PMMA slab photoluminescence decay at 1010 nm.