Electronic Suplimentry Infomration for

Rhenium(I) based metallocalix[4]arenes decorated with free functionalized benzimidazolyl unit†

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Contents

1. Experimental section

1.1. General Data. All starting materials and products were found to be stable toward moisture and air, and no specific precautions were taken to rigorously excluded air when conventional and solvothermal methods were used. Starting materials such as $Re_2(CO)_{10}$, H_2-thq, H_2-dhnq, 2-methylmercaptobenzimidazole and KOH were procured from commercial sources and used as received. Ligands, 2-thiophene-2-benzimidazole, 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene, H_2-bim can be easily prepared following previous reported methods.[S1] Elemental analyses were performed on a ElementarAnalysensysteme GmbH Vario EL-III instrument. FT-IR spectra were recorded on a Perkin-Elmer FTIR-2000 spectrometer. ^{1}H NMR spectra were recorded on a Jeol JNMECX-400P spectrometer. The electronic absorption spectra were recorded on a SPECORD 250-222P145 spectrophotometer at room temperature. The emission spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer at room temperature. The lifetime measurements were done on a Horiba JobinYvon Fluorocube at room temperature. The Photomultiplier tube voltage for fluorescence spectrophotometry was set at 600V using a slit width of 10 nm for both excitation and emission measurements. Spectroscopy grade solvents were used for all spectrophotometric measurements.

1.2. General procedure for synthesis of metallacycles. A mixture of $Re_2(CO)_{10}$, tritopic N-donors and bis-chelating units (H_2-bim/H_2-thq/H_2-dhnq) in toluene in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 48 h and then cooled to 25 °C. Good quality, dark-colored crystals were obtained and separated by filtration. The products werefiltered and washed with distilled hexane and air-dried.

1.3. Synthesis of [(Re(CO)$_3$)$_2$(bim)(L^2)] (1). A mixture of $Re_2(CO)_{10}$ (98.5 mg, 0.1509 mmol), L^2 (68.6 mg, 0.1057 mmol) and H_2-bim (21.5 mg, 0.1602 mmol) in toluene (10 mL) in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at

160 °C for 48 h and then cooled to 25 °C. Good quality, pale-yellow crystals were obtained and separated by filtration. The product was washed with distilled hexane and air-dried. Yield: 74 % (129.2 mg, 0.03767 mmol). Anal. Calcd for $C_{48}H_{40}N_{10}O_6S_3Re_2\cdot0.5C_7H_8$: C, 45.23; H, 3.24; N, 10.24; S, 7.03. Found: C, 44.93; H, 3.29; N, 10.04; S, 7.00. FT-IR (KBr, cm^{-1}): 2014, 1924, 1899, 1890, 1868 (C≡O). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61 (d, J = 8.04 Hz, 2H, H^{9},bim), 7.48 (d, J = 8.08 Hz, 2H, H$^{9'}$,bim),7.37 (d, J = 8.04 Hz, 2H, H^{4}benzimidazolyl), 7.30 (br, 2H, H$^{4'}$benzimidazolyl), 7.07-7.02 (m, 2H, H$^{5'}$, benzimidazolyl), 6.78 (t, J = 8.06 Hz, 2H, H^{6}, benzimidazolyl), 6.67 (t, J = 8.34 Hz, 2H, H$^{6',7}$, benzimidazolyl), 6.20 (d, J = 8.08 Hz, 2H, H$^{7'}$, 5.66 (s, 2H, H^{8}, methylene), 5.64 (s, 2 H, H$^{8'}$, methylene), 5.60 (s, 4 H, H^{8}, methylene), 5.57 (s, 4 H, H^{8a}, methylene), 5.42 (s, 2 H, H$^{8a'}$, methylene), 2.81(s, 6H, H^{1}, -SCH_3), 2.62 (s, 3H, H$^{1'}$, -SCH_3), 2.30 (s, 6H, H^{9}, -CH_3) and 2.20 (s, 3H, H$^{9'}$, -SCH_3).

1.4. Synthesis of [(Re(CO)$_3$)$_2$(L^2)(thq)] (2).The dark crystals of **2**were collected from $Re_2(CO)_{10}$ (99.7 mg, 0.1527 mmol), L^2(63.9 mg, 0.0985 mmol) and H$_2$-thq (29.7 mg, 0.1726 mmol) in toluene (10 mL). Yield: 74 % (129.2 mg, 0.03767 mmol). Anal. Calcd for $C_{48}H_{38}N_6O_{12}S_3Re_2\cdot C_7H_8$: C, 45.51; H, 3.19; N, 5.79; S, 6.63. Found: C, 45.72; H, 3.26; N, 6.09; S, 6.94. FT-IR (KBr, cm^{-1}): 2017 (C≡O) and 1890 (br, vs) (C≡O). ^{1}H NMR (400 MHz, DMSO-d_6)***immediately***: δ 7.54 (d, 2H, J = 8.08 Hz, H^{4}, benzimidazolyl), 7.48 (d, 4H, J = 8.08 Hz, H$^{4'}$, benzimidazolyl), 7.14 (t, 2H, H^{5}, benzimidazolyl), 7.08 (t, 4H, H$^{5'}$, benzimidazolyl), 6.98 (t, 2H, H^{6}, benzimidazolyl), 6.83 (m, 8H, H$^{6',7}$, benzimidazolyl), 6.83 (d, J = 8.08 Hz, 2H, H$^{7'}$, benzimidazolyl), 5.73 (d, J = 8.08 Hz, 3H, H^{8a}, methylene), 5.64 (d,J = 8.08 Hz, 3H, H$^{8a'}$, methylene), 5.40 (s, 6H, H^{8b}, methylene), (2.62 (s, 9H, H$^{1'}$, -SCH_3), and 2.18 (s, 9H, H^{9}, -CH_3).***After 20 days***:δ 7.48 (d, J = 8.24 Hz, 4H, H^{4}, benzimidazolyl), 7.24 (d, J = 7.36 Hz, 2H,H^{4}, benzimidazolyl), 7.16 (t, J = 7.56 Hz, 2H,H^{5}, benzimidazolyl), 7.05–7.09 (m, 2H, H^{5a}, benzimidazolyl), 6.76–6.83 (m, 2 H, $H^{6,7}$, benzimidazolyl), 5.42 (s, 6 H, H^{8}, methylene), 2.62 (s, 9H, $H^{1'}$, -SCH_3), and 2.18 (s, 9H, H^{9}, -CH_3).

1.5. Synthesis of [(Re(CO)$_3$)$_2$(L^2)(dhnq)] (3). The dark crystals of **3**were collected from $Re_2(CO)_{10}$ (101.2 mg, 0.1551 mmol), L^2(65.1 mg, 0.1003 mmol) and H_2-dhnq (45.2 mg, 0.1557 mmol) in toluene (10 mL). Yield: 82 % (132.7 mg, 0.08264 mmol). Anal. Calcd for $C_{60}H_{44}N_6O_{10}S_3Re_2 \cdot C_7H_8 \cdot 2H_2O$: C, 50.11; H, 3.52; N, 5.23; S, 5.99. Found: C, 49.89; H, 3.77; N, 4.87; S, 5.69. FT-IR (KBr, cm^{-1}): 2011 (vs) (C≡O) and 1881 (br, vs) (C≡O). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 (dd, J = 5.84 Hz, 2H, dhnq), 8.42-8.39 (m, 4H, dhnq), 8.33 (dd, J = 5.86 Hz, 2H, dhnq), 7.94-7.92 (m, 4H, dhnq), 7.89-7.86 (m, 2H, DHNQ), 7.82 (dd, J = 6.2 Hz, 2H, dhnq), 7.72 (d, J = 8.04 Hz, 4H$^{4,4'}$, benzimidazolyl), 7.57 (d, J = 8.04 Hz, H^{4a}, 2H, benzimidazolyl), 7.45 (d, J = 7.32 Hz, $H^{4a'}$, 2H, benzimidazolyl), 7.06 (t, J = 8.06 Hz, 2H, $H^{5,5'}$, benzimidazolyl), 6.82–6.75 (m, 2H, H^{5a}, benzimidazolyl), 6.68 (t, J = 7.68 Hz, 4H, $H^{5a',6,6'}$, benzimidazolyl), 6.59 (t, J = 7.70 Hz, 4H, $H^{6a,7a}$, benzimidazolyl), 6.32 (d, J = 8.80 Hz, 2 H, $H^{6a',7a'}$, benzimidazolyl), 5.56 (s, 4 H, H^{8}, methylene), 5.50 (s, 4 H, $H^{8a,}$, methylene), 5.46 (s, 2 H, $H^{8'}$, methylene), 5.41 (s, 2 H, $H^{8a'}$, methylene), 2.77 (s, 6H, H^{1}, -SCH_3), 2.62 (s, 2H, $H^{1'}$, -SCH_3), 2.59 (s, 9H, H^{1a}, -SCH_3), 2.47 (s, 6H, H^{9a}, -CH_3), 2.29 (s, 6H, H^{9}, -CH_3), 2.18 (s, 2H, $H^{9'}$, -CH_3).

1.6. Synthesis of [(Re(CO)$_3$)$_2$(L^3)(thq)] (4). The dark crystals of **4** were collected from $Re_2(CO)_{10}$ (98.1 mg, 0.1503 mmol), L^3 (83.1 mg, 0.1098 mmol) and H_2-thq (34.2 mg, 0.199 mmol) in toluene (10 mL). Yield: 75 % (121.2 mg, 0.0826 mmol). Anal. Calcd for $C_{57}H_{38}N_6O_{12}Re_2S_3 \cdot C_7H_8$: 49.28; H, 2.97; N, 5.39; S, 6.17. Found: C, 49.51; H, 2.86; N, 5.28; S, 6.09. FT-IR (KBr, cm^{-1}): 2017, 1891 (C≡O). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (m, 6H, $H^{a,c}$, thio), 7.59 (d, J = 8.04 Hz, 4H, $H^{5,8,5'8'}{}_{,}$ benzimidalolyl), 7.28-7.26 (m, 3H, H^{b}thio), 7.12 (t, J = 7.68 Hz, 4H, $H^{6,7,6'7'}$ benzimidazolyl), 6.64 (t, J = 7.70 Hz, 2H, $H^{6a,7a}$, benzimidazolyl), 6.28 (d, *J* = 8.04 Hz, 2H, $H^{5a,8a}$, benzimidazolyl), 5.74 (s, 6H, H^9, methylene), 1.99 (s, 9H, H^{10}, -CH_3).

1.7. X-ray Crystallography.Intensity data of suitably sized crystals of **1-4** were collected on an Oxford Xcalibur S diffractometer (4-circle *κ*goniometer, Sapphire-3 CCD detector, ω scans, graphite monochromator, and a single wavelength Enhance X-ray source with MoK*α*radiation).[S2a] Pre-experiment, data collection, data reduction and absorption corrections were performed with the CrysAlisPro software suite.[S2b] The structures were solved by direct methods using SIR 92,[S2c] which revealed the atomic positions, and refined using the SHELX-97 program package[S2d] and SHELXL-97 (within the WinGX program package).[S2d-2f] Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model.The detailed crystallographic data's of **1**–**4** are given in Table S1.

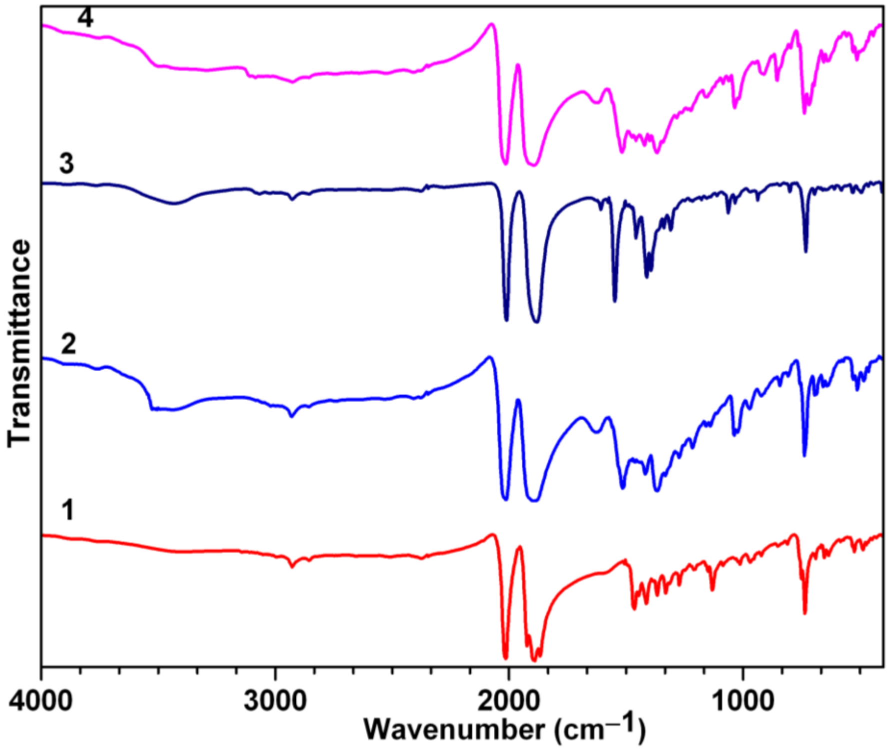

Fig. S1 FT-IR spectra of **1-4** in KBr.

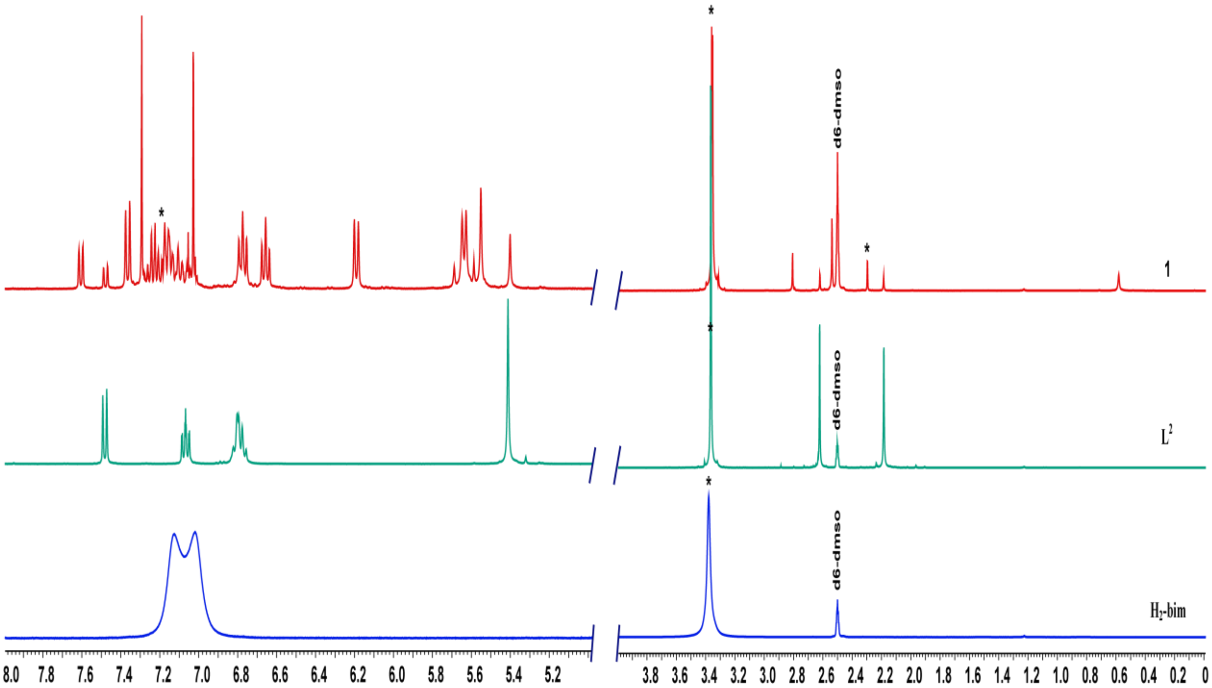

Fig S2 ^{1}H NMR spectra of free ligands and **1** in DMSO-d_6 (* = solvent and solvent water peaks).

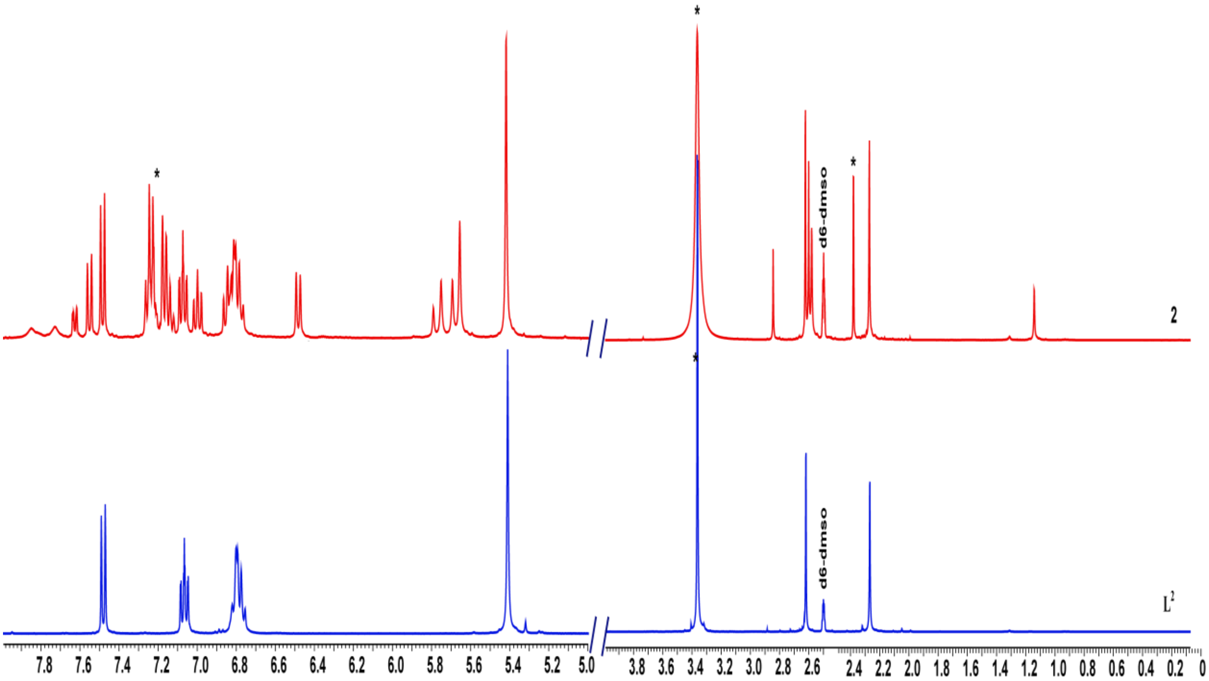

Fig S3 ^{1}H NMR spectra of free ligand and **2** in DMSO-d_6 (* = solvent and solvent water peaks).

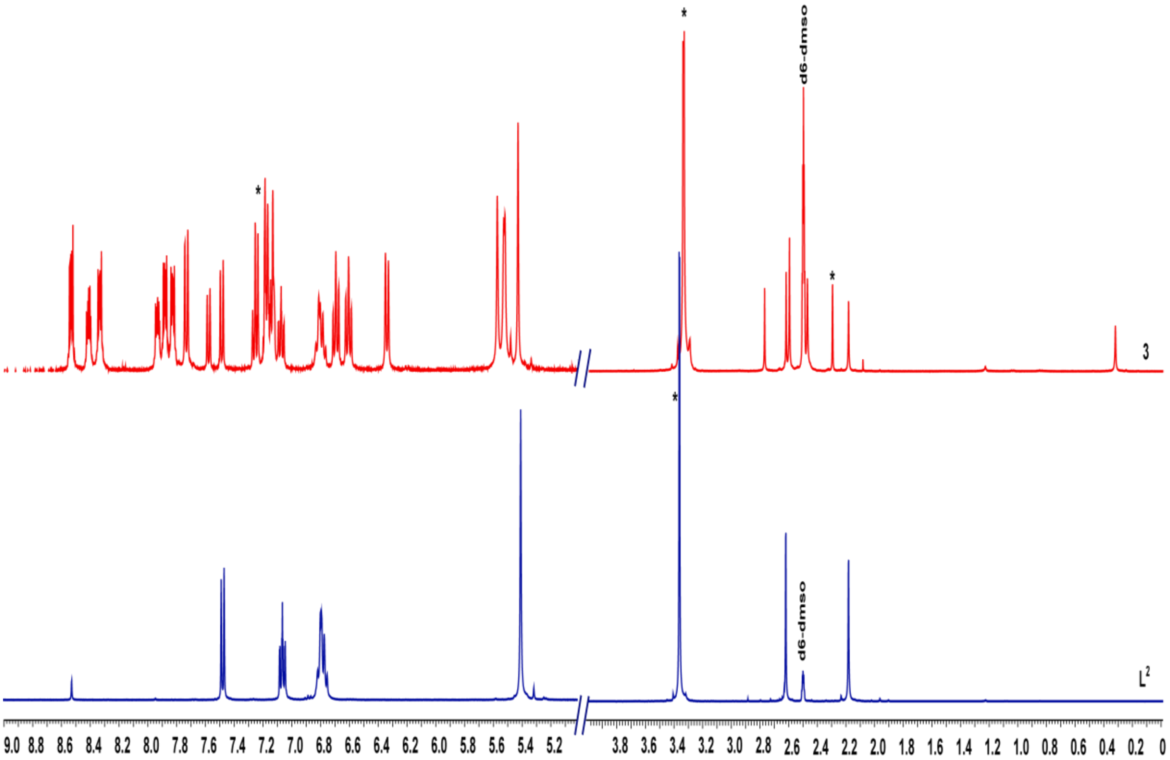

Fig S4 ^{1}H NMR spectra of free ligand and **3** in DMSO-d_6 (* = solvent and solvent water peaks).

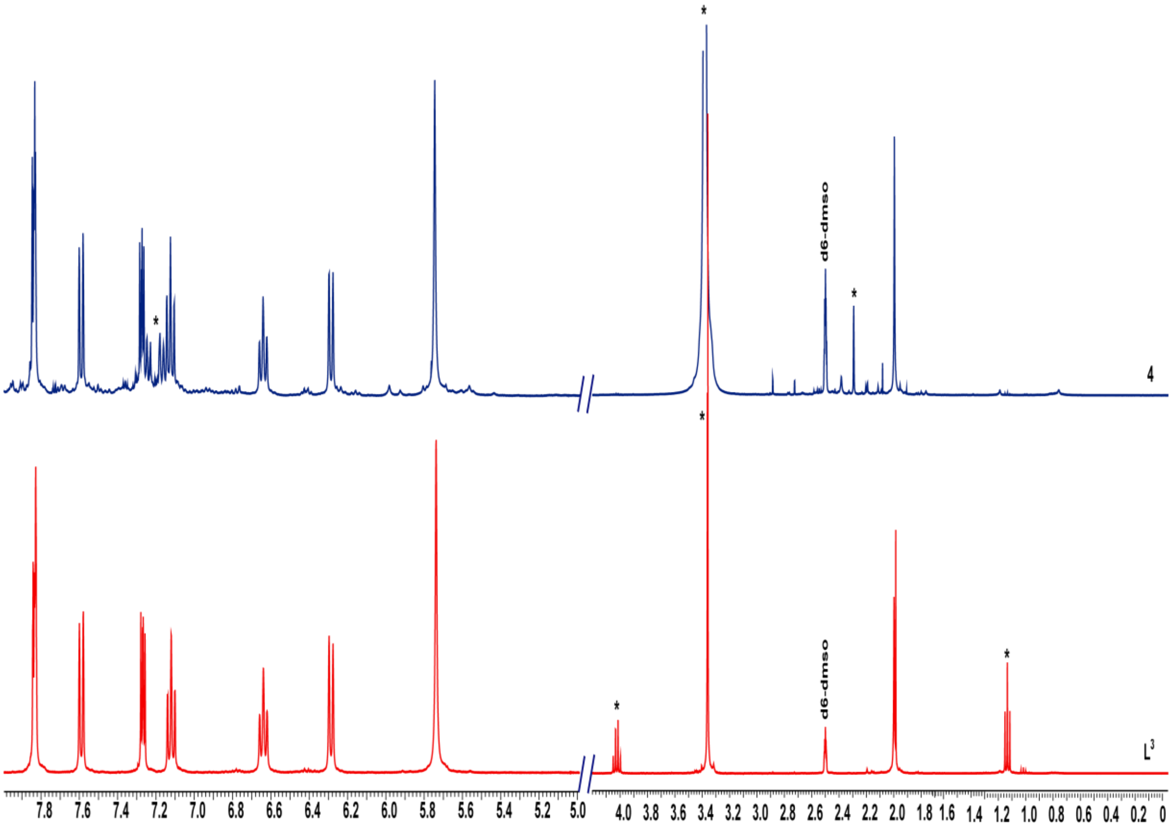

Fig S5 ^{1}H NMR spectra of free ligand and **4** in DMSO-d_6 (* = solvent and solvent water peaks).

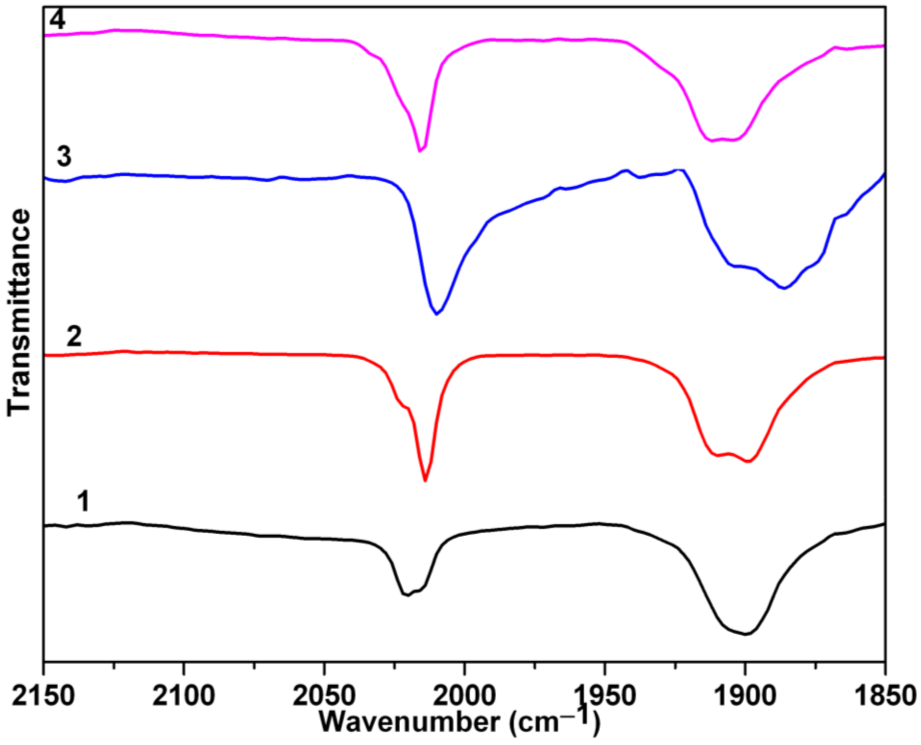

Fig. S6 Partial FT-IR spectra of **1-4** in acetone.

Table S1 The crystallographic data of **1-4**.

	1	**2**	**3**	**4**
Formula	$C_{52}H_{40}N_{10}O_6Re_2S_3$	$C_{48}H_{38}N_6O_{12}Re_2S_3$	$C_{127}H_{96}N_{12}O_{20}Re_4S_6$	$C_{57}H_{38}N_6O_{12}Re_2S_3$
M_r	1369.52	1359.42	3047.32	1467.57
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$	$P2_1/c$
a (Å)	13.1042(4)	12.8639(2)	28.6866(15)	23.346(3)
b (Å)	13.4573(4)	21.2643(4)	18.3837(9)	13.6127(9)
c (Å)	14.6018(5)	21.5350(4)	25.0892(14)	18.1764(16)
α(°)	91.058(3)	107.672(2)	90.00	90.00
β(°)	93.181(3)	90.2800(10)	111.660(6)	110.725(12)
γ(°)	101.095(3)	100.230(2)	90.00	90.00
V (Å^3)	2521.85(14)	5512.64(17)	12296.9(11)	5402.8(8)
Z	2	4	4	4
T (K)	293(2)	295(2)	293(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	1.804	1.638	1.646	1.804
μ(Mo Kα) (mm^{-1})	4.981	4.563	4.099	4.663
F(000)	1336	2648	5992	2863
parameters	664	1291	1494	718
no. of reflns collected	39562	85834	180182	59145
no. of reflns used	12108	26285	25113	13288
R1[a]/wR2[b] [$I > 2\sigma(I)$]	0.0267/0.0552	0.0607/0.1580	0.0671/0.1593	0.1023/0.2030
R1[a]/wR2[b] (all data)	0.0365/0.0597	0.0923/0.1723	0.1214/0.1862	0.1563/ 0.2268
GooF[c]	1.033	1.060	1.041	1.154
largest residuals (e Å^{-3})	0.818 /-0.698	3.264 /-1.398	2.992/-1.089	4.856/-1.215

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

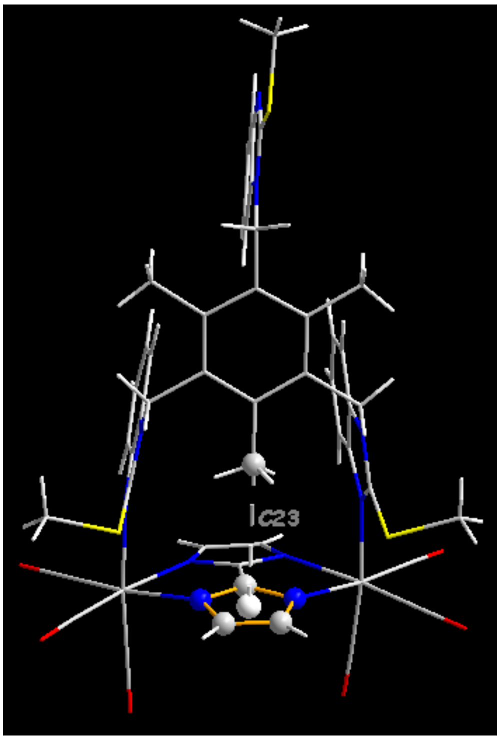

Fig. S7 Metallocalix[4]arene **1** shows intramolecular C–H···π interaction.

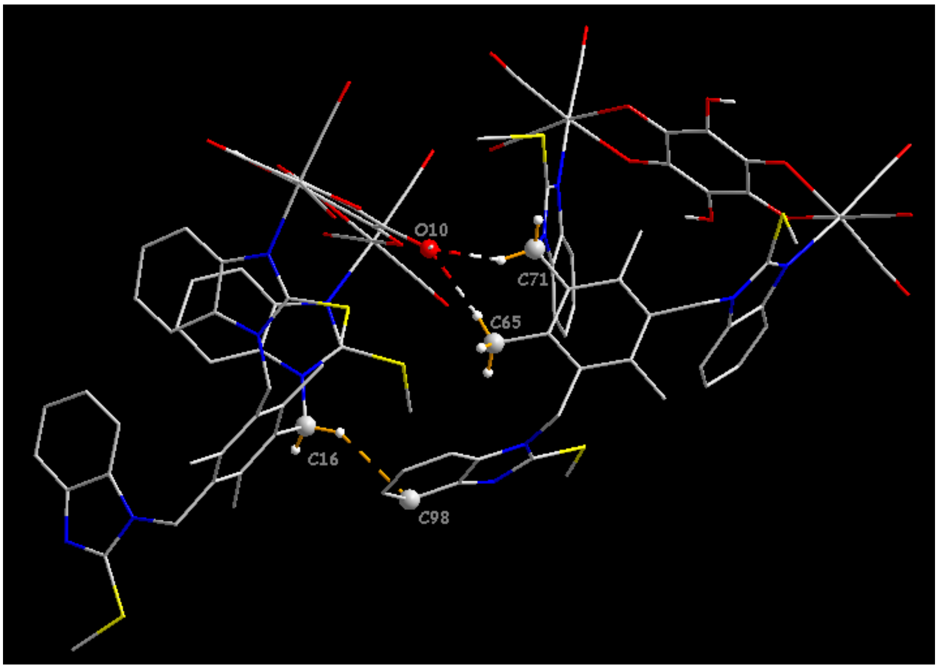

Fig. S8 Metallocalix[4]arene **2** shows intermolecular C–H···O and C–H···π interactions.

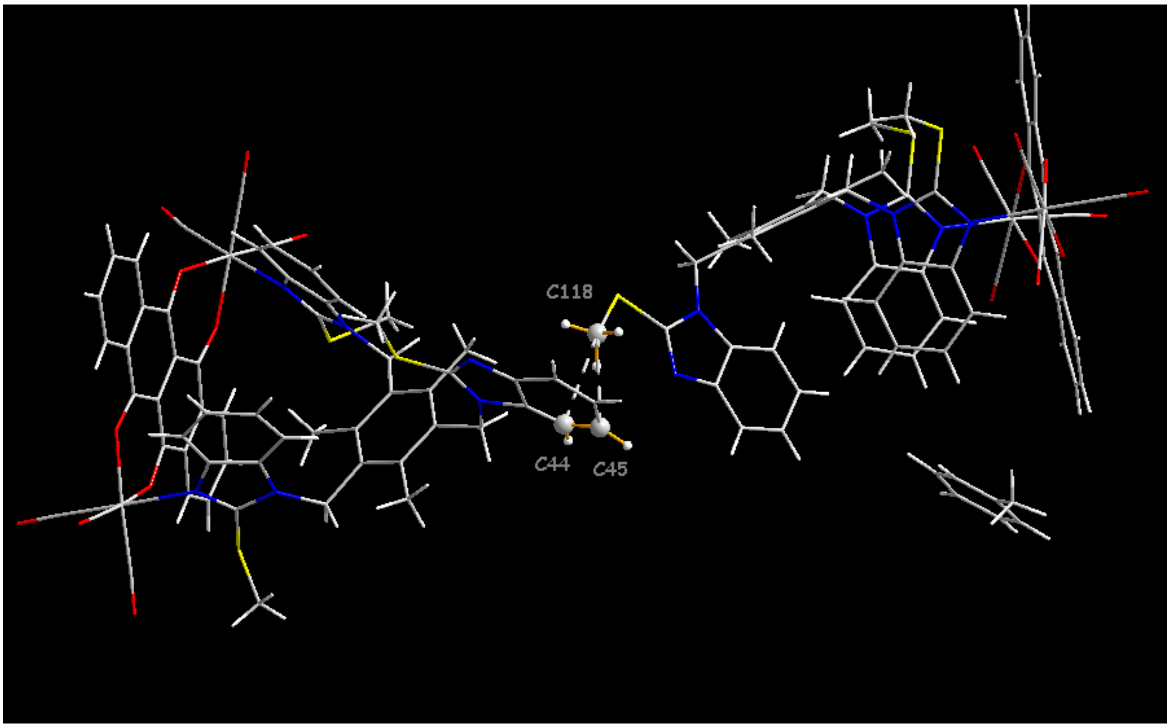

Fig. S9 Metallocalix[4]arene **3** shows intermolecular C–H···π interactions.

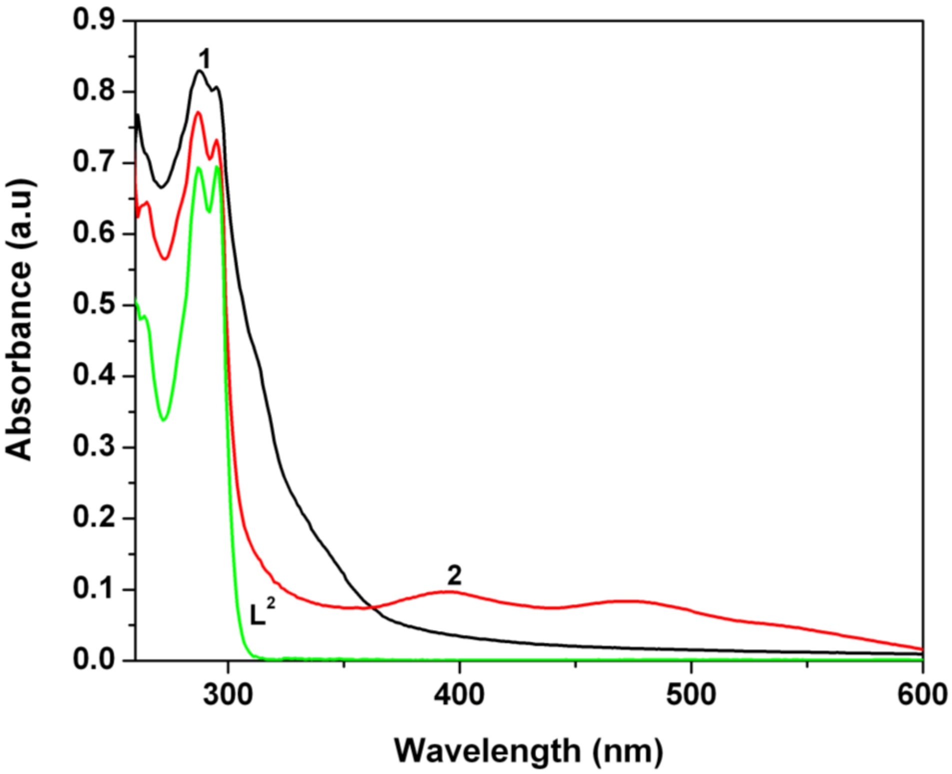

Fig. S10 UV-Vis spectra of free ligand and **1-2** in DMSO.

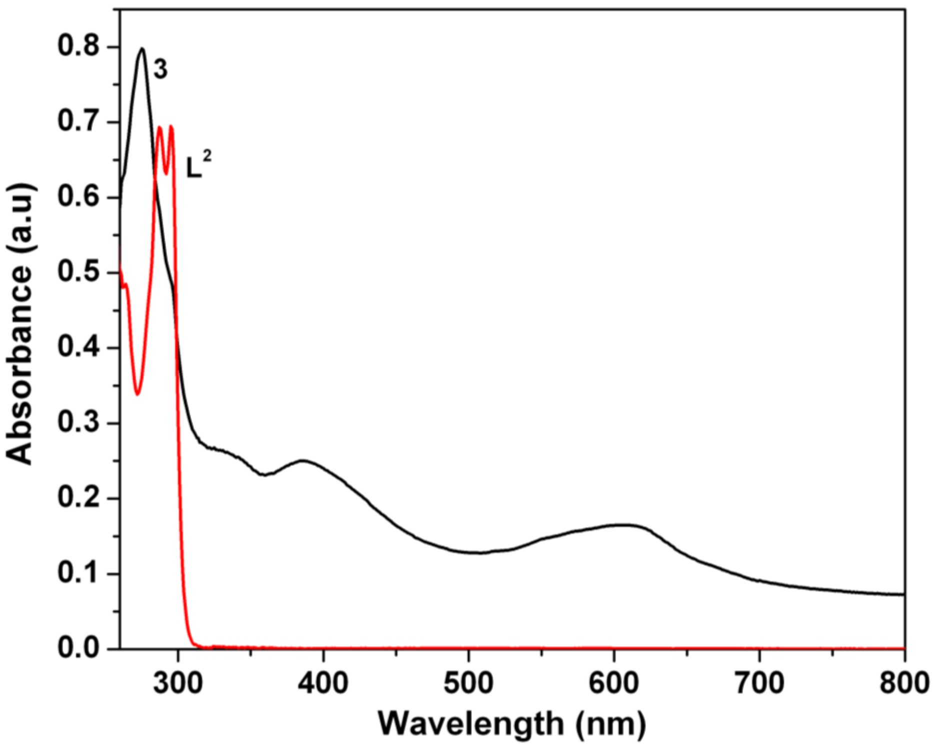

Fig. S11 UV-Vis spectra of free ligand and **3** in DMSO.

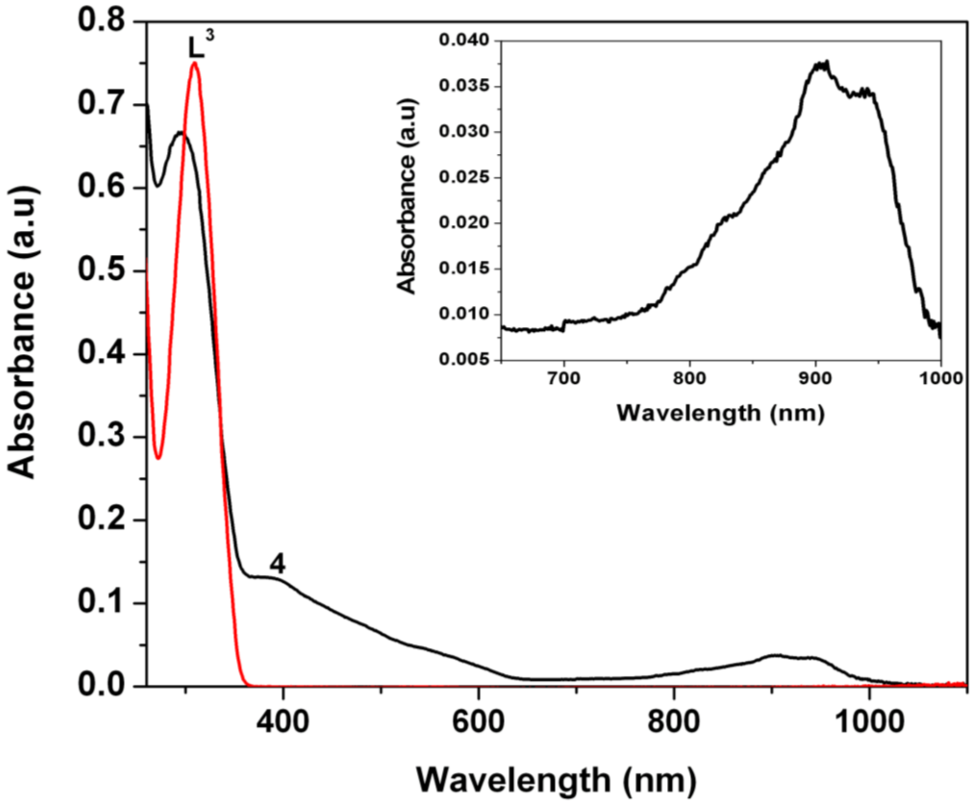

Fig. S12 UV-Vis spectra of free ligand and **4** in DMSO.

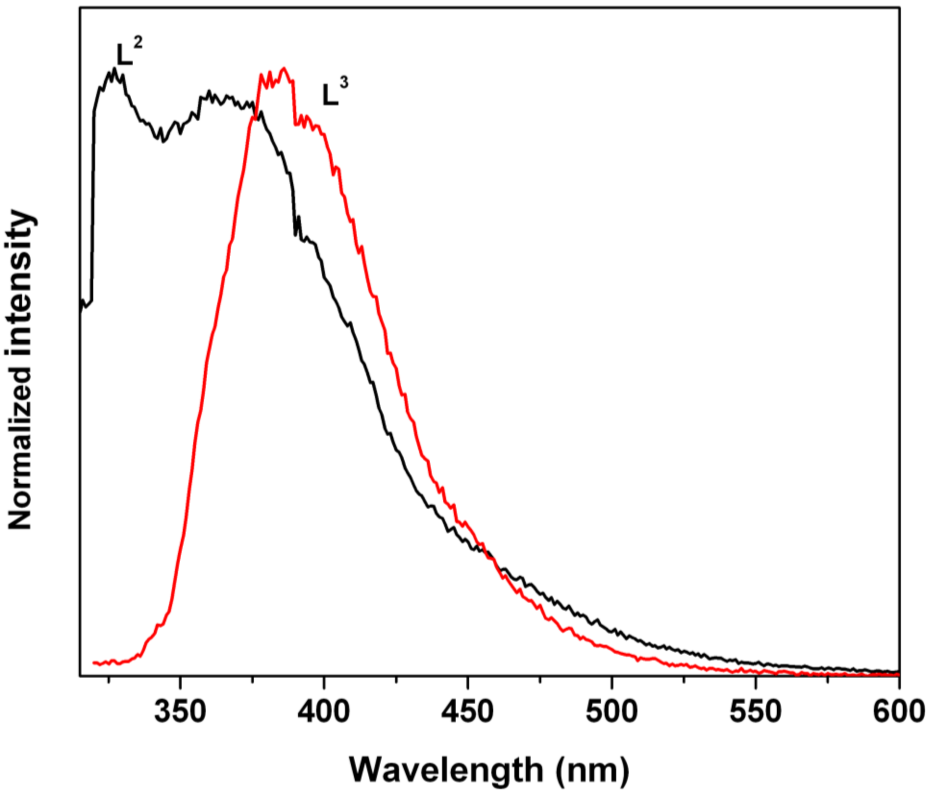

Fig. S13 Emission spectra of $\mathbf{L^2}$ and $\mathbf{L^3}$ in DMSO.

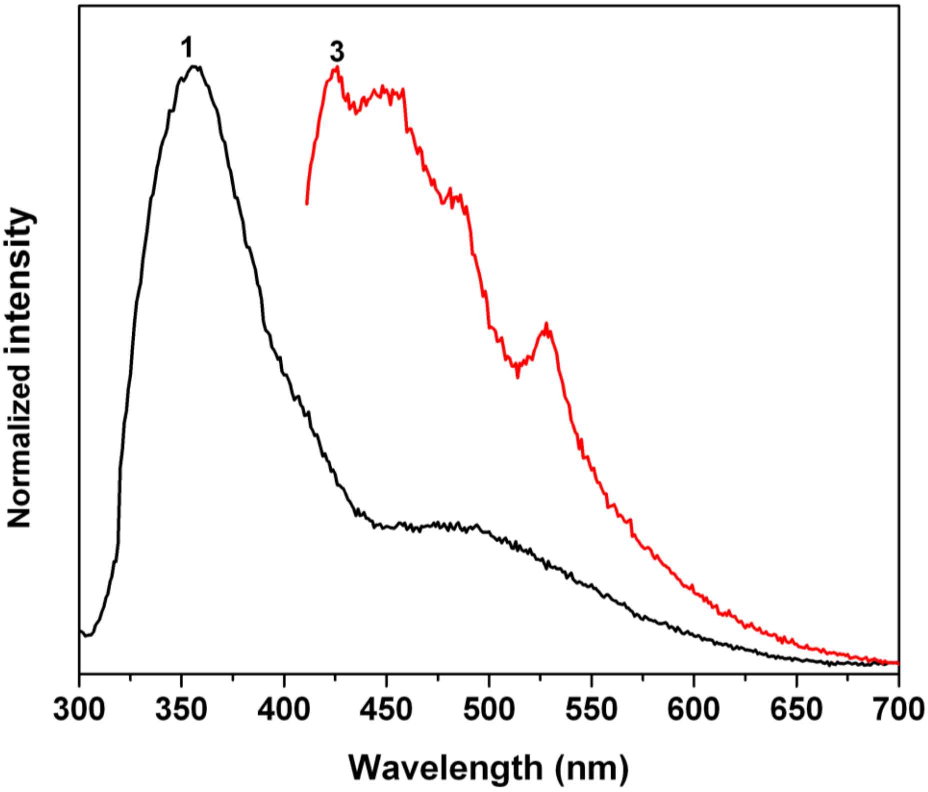

Fig. S14 Emission spectra of **1** and **3** in DMSO.

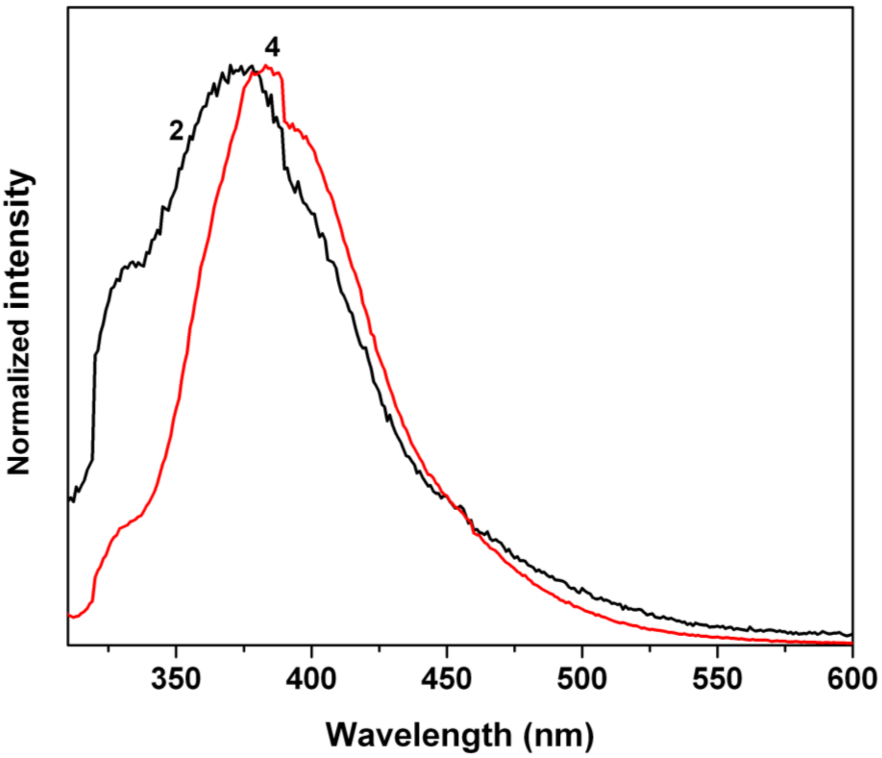

Fig. S15 Emission spectra of **2** and **4** in DMSO.

Table S2. Photophysical properties of ligands **L^2** and **L^3** in DMSO.

Ligands	λ_{abs}[nm]	λ_{em}[nm]
L^2	288	322
	295	325
		362
L^3	309	386

Table S3. UV-Vis absorption of complexes **1-4** in DMSO.

Complexes	λ_{abs}[nm] (ε, M^{-1}cm^{-1})
1	289 (33,882), 295 (33,099)
2	287 (57,870), 295 (54,796), 394 (6546), 473 (4362), 524 (3230)
3	275 (18,331), 334 (5949), 385 (5714), 606(3836)
4	296 (17,394), 400 (3284), 909 (998), 941 (933)

Table S4. Emission lifetimes of **L^2** and **L^3** in DMSO at 298 K.

Ligands	(α_1)	τ_1, ns	(α_2)	τ_2, ns	(α_3)	τ_3, ns	χ_r^2 [e]
L^{2}[a]	(0.95)	0.028±0.003	(0.04)	3.75±0.056	-	-	1.0003
L^{2}[b]	(0.97)	0.02 ±0.004	(0.02)	3.17±0.06	-	-	1.0169
L^{2}[c]	(0.26)	1.58±0.017	(0.66)	0.04±0.003	(0.07)	8.88±0.13	1.0184
L^{3}[d]	(1.00)	1.28±0.002	-	-	-	-	1.0011

α is the fractional amplitude, and τ is the lifetime for each component.

[a] Emission wavelength at 322 nm.

[b] Emission wavelength at 325 nm.

[c] Emission wavelength at 362 nm.

[d] Emission wavelength at 386 nm.

[e] Reduced χ_r^2 parameter ($\chi_r^{2)}$) indicating the goodness of the fit to the data.

Table S5. Emission data of **1-4**.

Complexes	λ_{exc}[nm]	λ_{em}[nm]
1	295	355, 488
2	295	374
3	275	379, 583
	385	426, 453, 486, 528
4	296	383

Table S6. Emission lifetimes of **1-4** in DMSO at 298 K.

compound	(α_1)	τ_1, ns	(α_2)	τ_2, ns	(α_3)	τ_3, ns	χ_r^2 [e]
1[a]	(0.49)	1.046±0.039	(0.50)	2.36±0.056	-	-	1.0014
2[b]	(0.58)	1.44 ±0.014	(0.11)	0.12±0.009	(0.3)	13.2±0.26	1.3359
3[c]	(0.38)	3.72±0.829	(0.55)	20.2±4.05	(0.06)	1.20±0.114	1.0387
4[d]	(1.00)	1.25±0.002	-	-	-	-	1.1080

α is the fractional amplitude, and τ is the lifetime for each component.

[a] Emission wavelength at 350 nm.

[b] Emission wavelength at 365 nm.

[c] Emission wavelength at 379 nm.

[d] Emission wavelength at 383 nm.

[e] Reduced χ_r^2 parameter ($\chi_r^{2)}$) indicating the goodness of the fit to the data.

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