

Supplementary Information

LMCT Facilitated Room Temperature Phosphorescence and Energy Transfer in Substituted Thiophenolates of Gd and Yb

Vasily A. Ilichev,^a Anton V. Rozhkov,^a Roman V. Romyantsev,^a Georgy K. Fukin,^a Ivan D. Grishin,^b Artem V. Dmitriev,^c Dmitry A. Lypenko,^c Eugeny I. Maltsev,^c Artem N. Yablonskiy,^d Boris A. Andreev^{b,d} and Mikhail N. Bochkarev^{a,b}

a G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina st. 49, 603950 Nizhny Novgorod, Russian Federation

b Nizhny Novgorod State University, Gagarina avenue 23/2, 603950 Nizhny Novgorod, Russian Federation

c A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Leninsky prospect 31, 199071 Moscow, Russian Federation

d Institute for Physics of Microstructures of Russian Academy of Sciences, 7 ul. Akademicheskaya, 603950 Nizhny Novgorod, Russian Federation

Supporting Information Contents

Synthesis of compounds 1-4	1
X-ray extended information	2
PL, PLE and absorption spectra of thiophenols SSN(H) and OSN(H)	5
MALDI-TOF spectra of 1-4 complexes	5
Proposed energy transfer scheme	7
V-J-L characteristics of OLEDs	8

Synthesis of compounds **1-4**

Synthesis of Gd₂(OSN)₆ (**1**)

A mixture of 2-(2'-mercaptophenyl)benzoxazole (OSN(H)) (150 mg, 0.66 mmol) and Gd[N(SiMe₃)₂]₃ (140 mg, 0.22 mmol) in DME (10 ml) was stirred at room temperature for 2 hours. Then solvent and volatile products were removed. The remaining residue was washed with hexane and recrystallized from DME. To eliminate residual DME precipitated yellow crystals were dried for 3 hours at 100 °C in vacuum to give **1** as yellow powder (128 mg, 70%). Elemental analysis: found C, 56.00; H, 2.85; N, 5.05; S, 11.54; Gd, 18.82 for C₃₉H₂₄N₃O₃S₃Gd: C, 56.03; H, 2.89; N, 5.03; S, 11.50; Gd, 18.80. IR (Nujol, cm⁻¹): 1607 (w), 1588 (m), 1536 (m), 1243 (s), 1196 (w), 1044 (m), 1034 (s), 1003 (w), 815 (s), 759 (m), 745 (s).

Synthesis of Gd(SSN)₃ (**2**)

The compound was synthesized similarly to **1** from 2-(2'-mercaptophenyl)benzothiazole (SSN(H)) (161 mg, 0.66 mmol) and Gd[N(SiMe₃)₂]₃ (140 mg, 0.22 mmol) to give **2** as yellow powder (142 mg, 73%). Elemental analysis: found C, 52.94; H, 2.75; N, 4.77; S, 21.76; Gd, 17.73 for C₃₉H₂₄N₃S₆Gd: C, 52.97; H, 2.74; N, 4.75; S, 21.75; Gd, 17.78. IR (Nujol, cm⁻¹): 1582 (w), 1561 (w), 1546 (w), 1439 (m), 1413 (w), 1287 (w), 1210 (s), 1129 (w), 1065 (w), 1038 (m), 973 (s), 857 (w), 756 (s), 701 (m).

Synthesis of Yb₂(OSN)₆ (**3**)

The compound was synthesized similarly to **1** from 2-(2'-mercaptophenyl)benzoxazole (OSN(H)) (150 mg, 0.66 mmol) and Yb[N(SiMe₃)₂]₃ (144 mg, 0.22 mmol) to give **3** as orange powder (142 mg, 75%). Elemental analysis: found C, 54.93; H, 2.82; N, 4.94; S, 11.26; Yb, 20.30 for C₃₉H₂₄N₃O₃S₃Yb: C, 54.99; H, 2.84; N, 4.93; S, 11.29; Yb, 20.31. IR spectrum of **3** is identical to that of **1**.

Synthesis of Yb(SSN)₃ (**4**)

The compound was synthesized similarly to **1** from 2-(2'-mercaptophenyl)benzothiazole (SSN(H)) (161 mg, 0.66 mmol) and Yb[N(SiMe₃)₂]₃ (144 mg, 0.22 mmol). The main difference of this synthesis was precipitation of two types of crystals. Orange crystals of **4** were manually separated from yellowish ones (which are bis[2-(2-benzothiazolyl)phenyl]disulfide) and dried to give **4** as orange powder (89 mg, 45%). Elemental analysis: found C, 52.00; H, 2.66; N, 4.70; S, 21.39; Yb, 19.25 for C₃₉H₂₄N₃S₆Yb: C, 52.04; H, 2.69; N, 4.67; S, 21.37; Yb, 19.23. IR spectrum of **4** is identical to that of **2**.

X-ray extended information

Table 1S. Details of crystallographic, collection and refinement data for **3** and **4**.

Complex	4	3
Empirical formula	C ₄₃ H ₃₄ N ₃ O ₂ S ₆ Yb	C ₈₆ H ₆₈ N ₆ O ₁₀ S ₆ Yb ₂
Formula weight	990.13	1883.90
Temperature [K]	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic
Space group	Pna2 ₁	P2 ₁ /c
Unit cell dimensions		
a[Å]	17.7938(14)	16.6185(12)
b[Å]	10.9568(9)	20.4855(14)
c[Å]	20.0462(15)	24.5176(17)
α[°]	90	90
β[°]	90	101.251(2)
γ[°]	90	90
Volume [Å ³]	3908.3(5)	8186.3(10)
Z	4	4
Calculated density [Mg/m ³]	1.683	1.529
Absorption coefficient	2.756	2.485

[mm ⁻¹]		
Crystal size [mm]	0.50×0.30× 0.23	0.56×0.29× 0.26
θ [°]	2.183 - 30.490	2.293 - 26.000
Reflections collected / unique	54477 / 11852	77971 / 15989
R_{int}	0.0464	0.0421
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0255,$ $wR_2=0.0525$	$R_1=0.0564,$ $wR_2=0.1241$
R indices (all data)	$R_1=0.0327,$ $wR_2=0.0549$	$R_1=0.0624,$ $wR_2=0.1264$
S	1.024	1.072
Largest diff. peak and hole [e/Å ³]	1.535/-1.161	2.096/-2.392

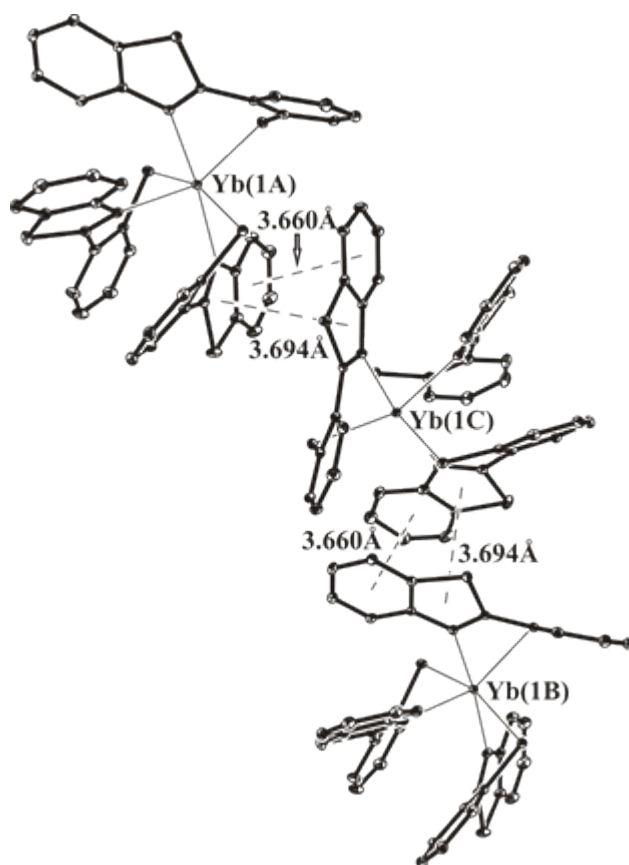
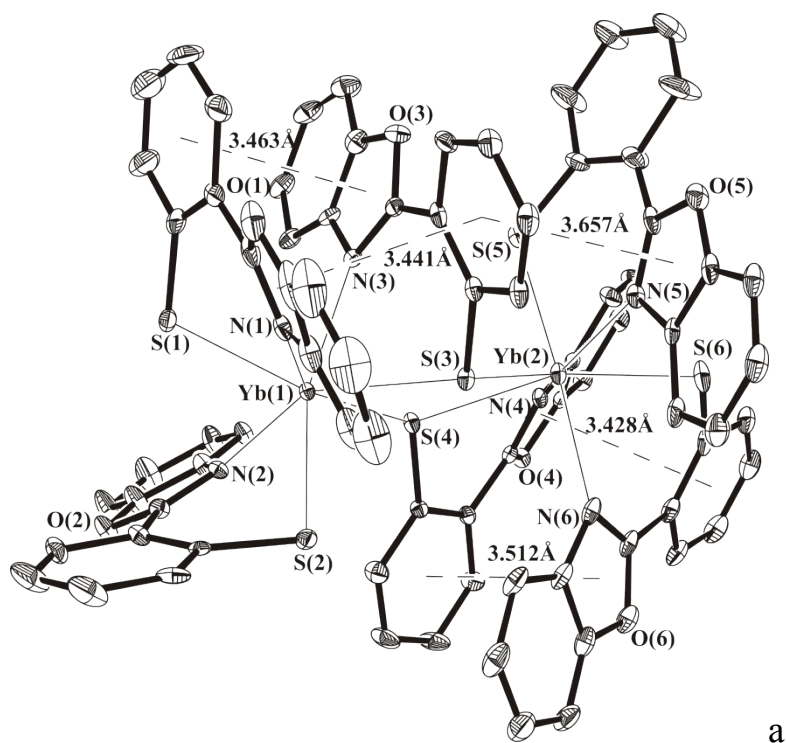
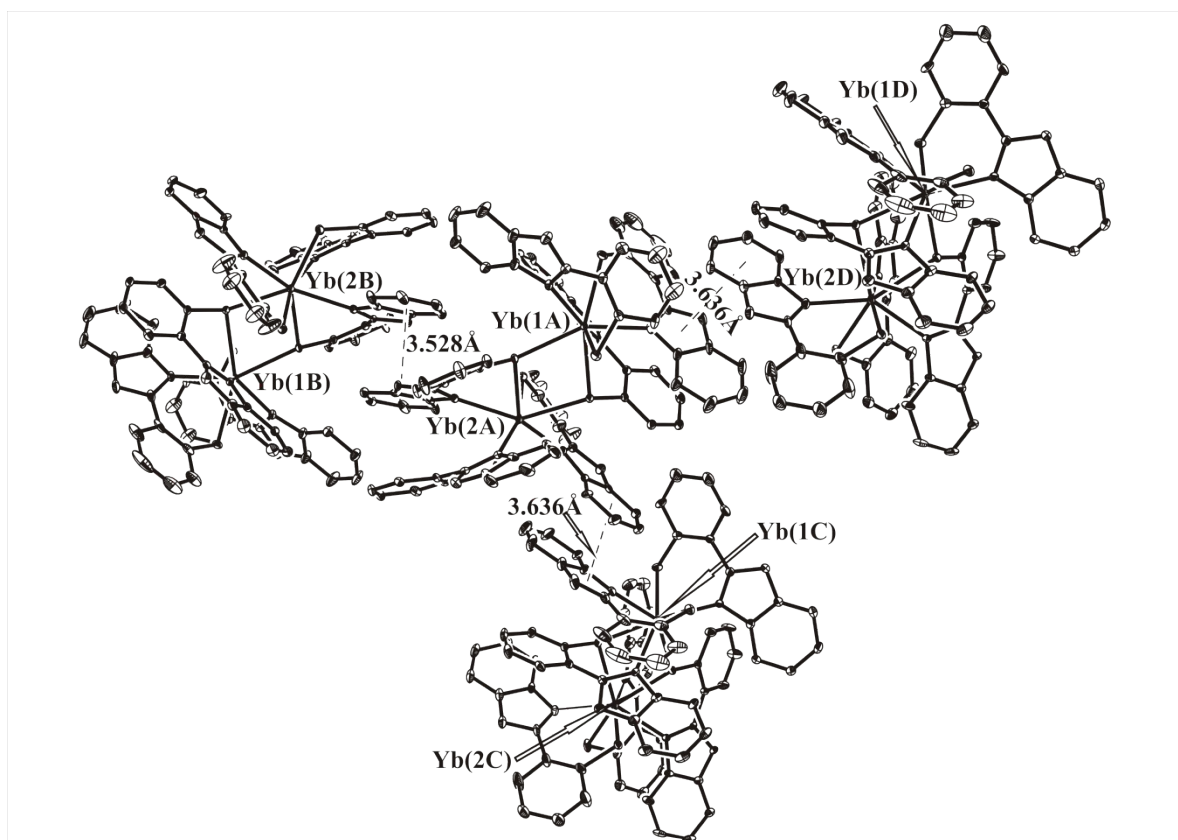


Figure 1S. Fragment of crystal packing of **4** containing $\pi \dots \pi$ interaction.



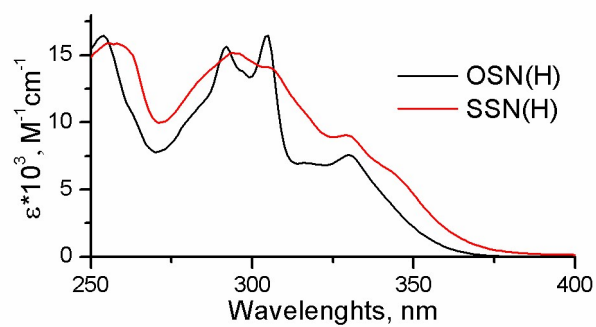
a



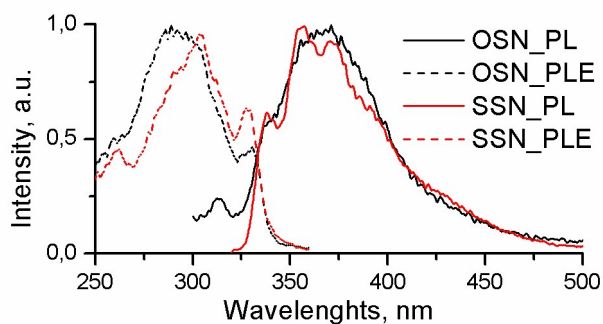
b

Figure 2S. Intramolecular (a) and intermolecular (b) π ... π interactions in **3**.

PL, PLE and absorption spectra of thiophenols SSN(H) and OSN(H)



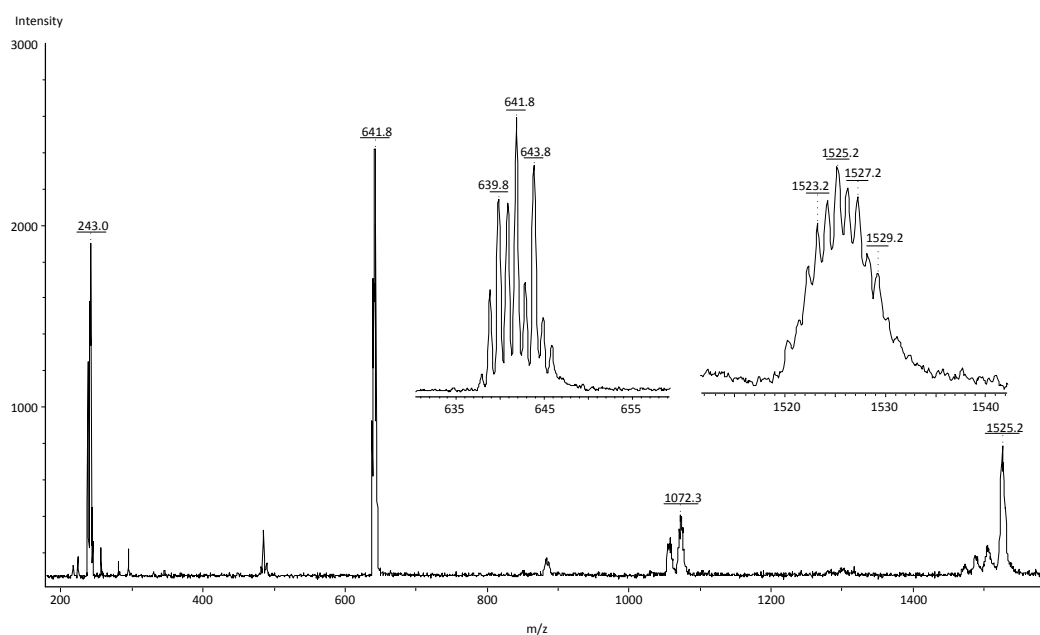
a



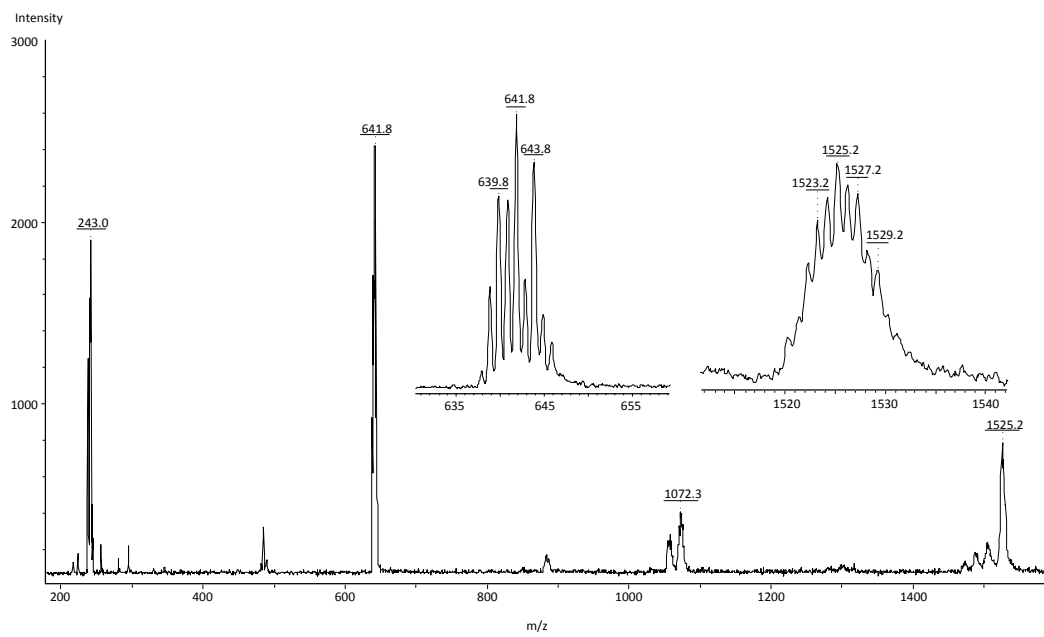
b

Figure 3S. Absorption (a), PL and PLE (b) spectra of thiophenols SSN(H) and OSN(H).

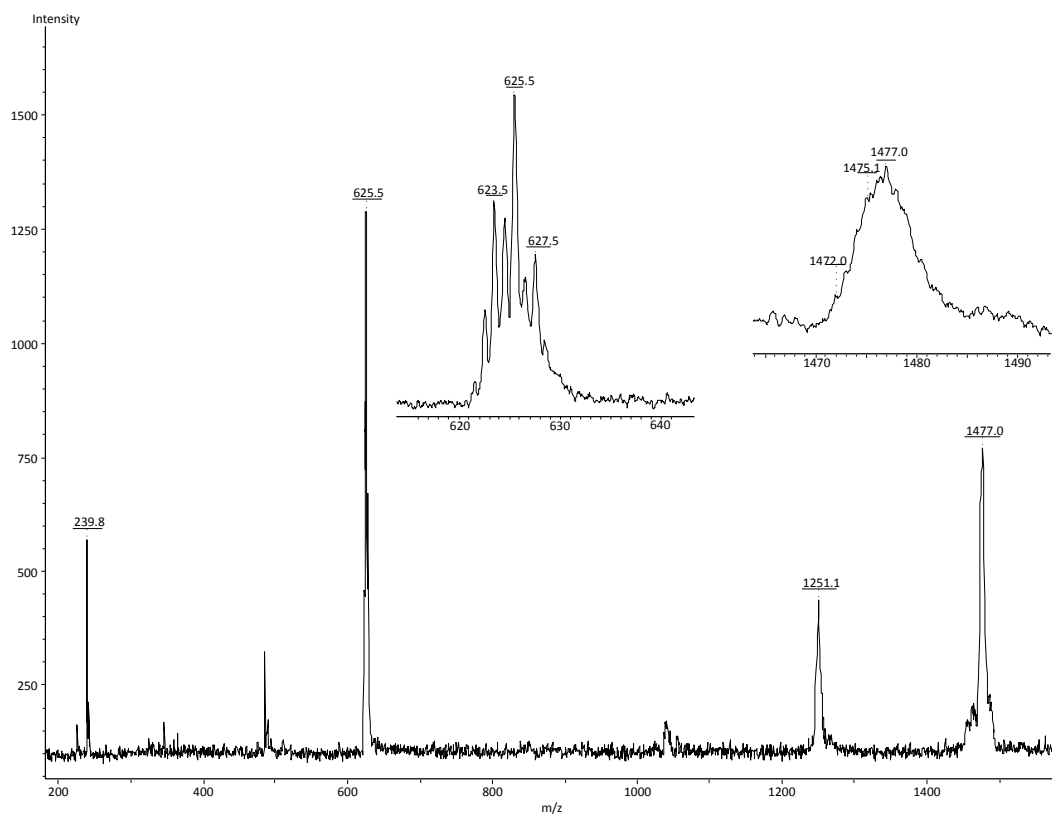
MALDI-TOF spectra of 1-4 complexes



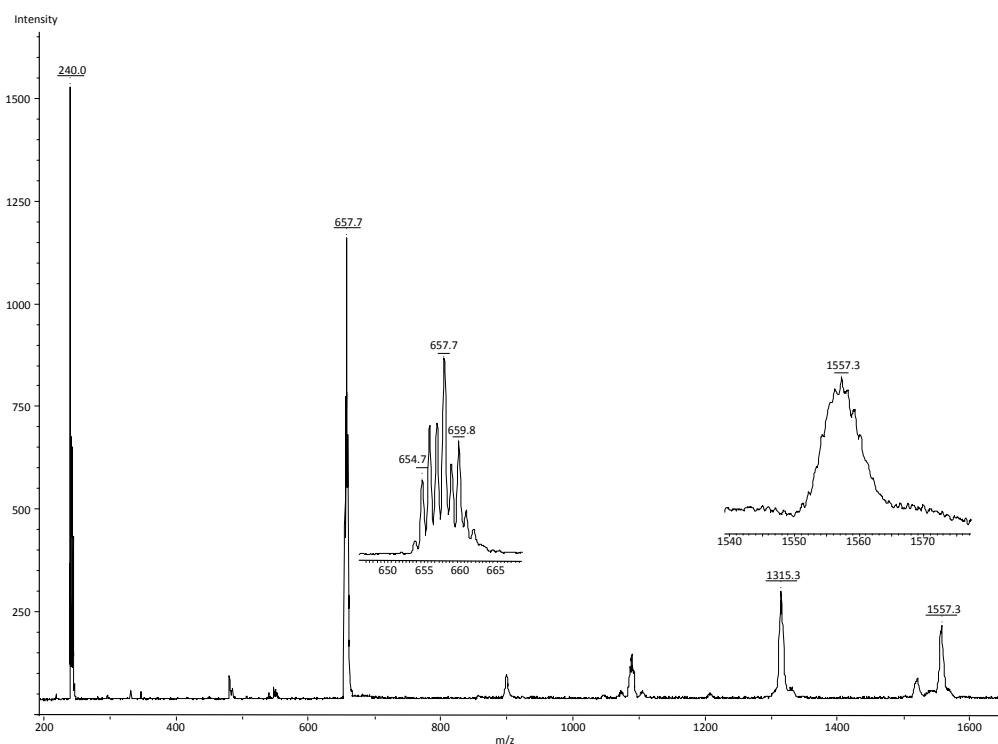
a



b



c

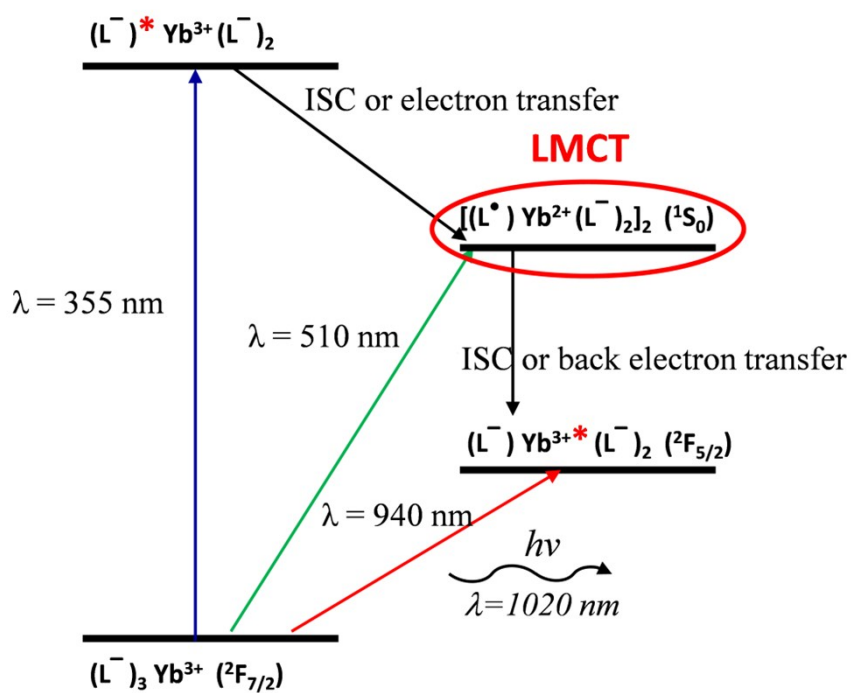


d

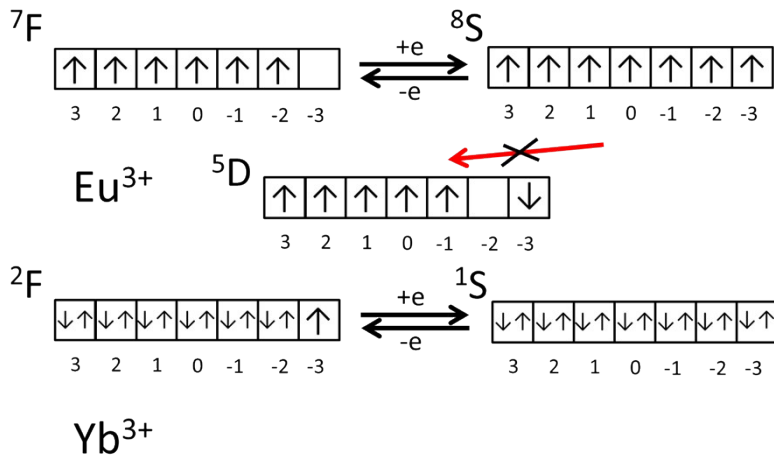
Figure 4S. MALDI-TOF spectra of compounds **1** (a), **2** (b), **3** (c), **4** (d).

Proposed energy transfer scheme

Scheme 1S. Proposed scheme of energy transfer in the Yb complexes (a) and 4f configurations of Eu and Yb in trivalent and divalent state (b).

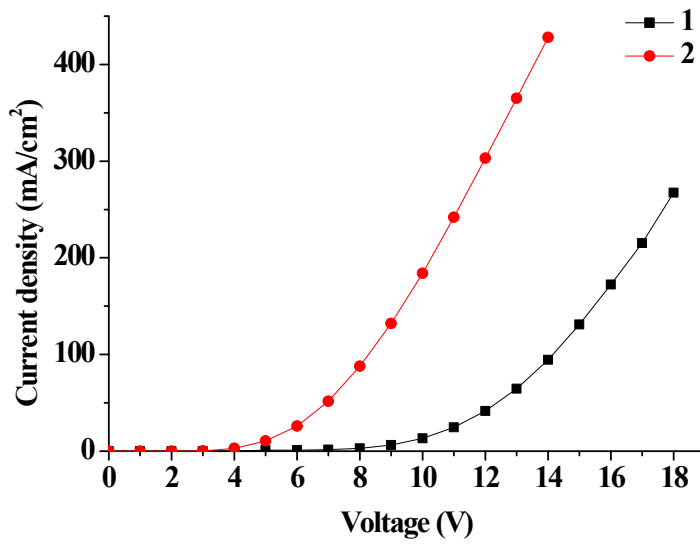


(a)

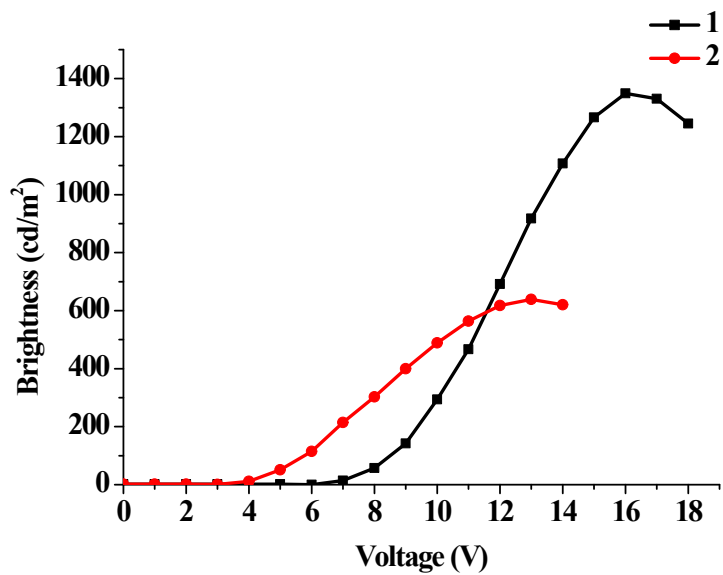


(b)

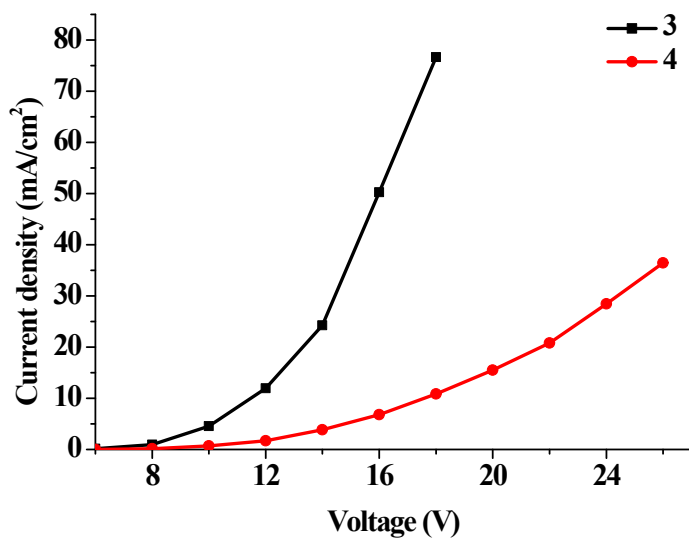
V-J-L characteristics of OLEDs



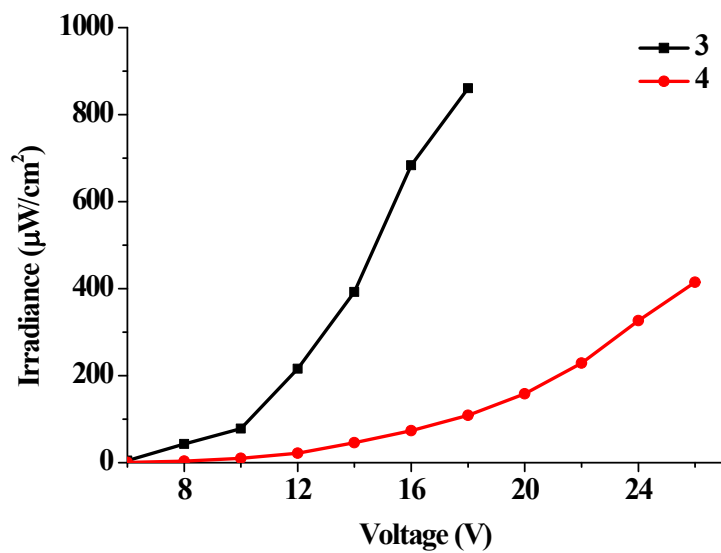
a



b



c



d

Figure 5S. V-J (a) and V-L (b) characteristics of **1** and **2**; V-J (c) and V-L (d) characteristics of **3** and **4**.