Electronic supplementary information

Recent advances in energy transfer in bulk and nanoscale luminescent materials: From spectroscopy to applications

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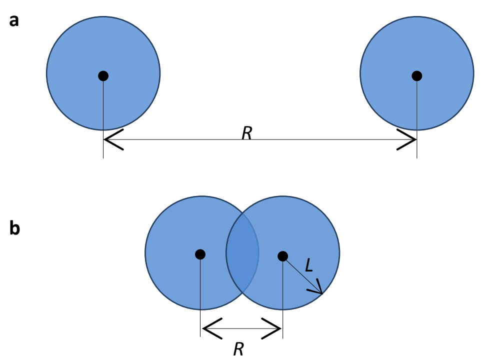

Fig. S1 Resonance ET by (a) dipole and multipole interaction, and (b) exchange interaction. It shows that the exchange interaction requires the overlap of wavefunctions of the two centers while the dipole or multipole interactions do not.

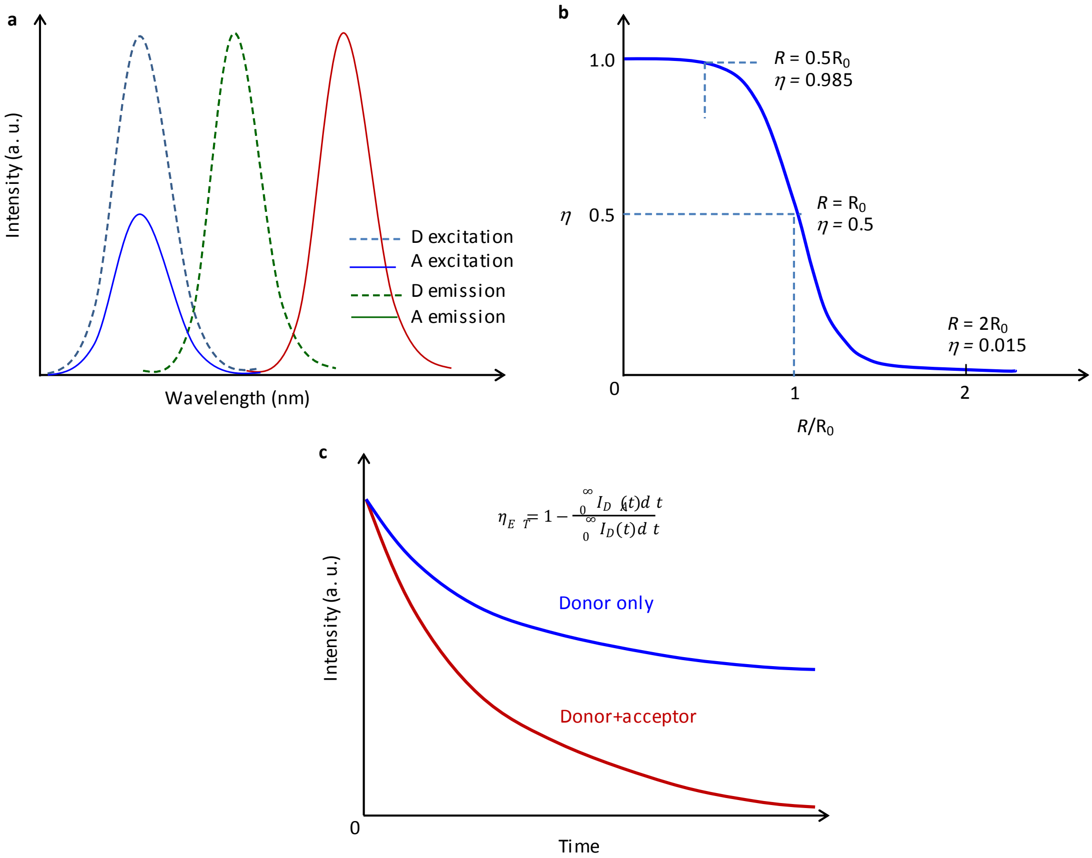

Fig. S2 Experimental observation of sensitized luminescence in donor-acceptor pair. (a) Typical experimental spectra for donor (D) and acceptor (A). The overlap in the excitation spectra of D and A is regarded as a direct evidence of sensitized emission, because the excitation of D leads to the emission of A. (b) Dependence on ET efficiency (η) on D-A separation. R_0 is the critical distance where ET rate equals radiative rate of D. (c) Fluorescence decay curves for the donor in the absence and presence of acceptor. The energy transfer efficiency can be calculated from the curves.

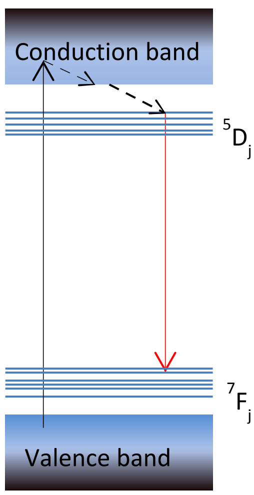

Fig. S3 Representative mechanism for host sensitized luminescence of Eu^{3+} emission by the transition of $^5D_j \rightarrow {}^7F_j$. UV excitation promote an electron from the valence band to the conduction band. Followed by energy migration (mediated by excitons), the excitation energy is then transferred to 4f levels of Eu^{3+} ions, finally giving the reddish emission.

Table S1 Selected examples of host sensitized luminescence in practical luminescence materials activated with RE or TM metal ions*.

Phosphor	Host absorption	Emission color/position nm
YVO_4:Eu	< 420 nm	Red / 620 nm
$CaMoO_4$:Eu	< 350 nm	Red/ 600 nm, 614 nm
Y_2O_2S:Eu	< 400 nm	Orange/Multiple peaks from 500 to 650 nm
$PbWO_4$	-----	Blue / 420 nm
$Bi_4Ge_3O_{12}$	< 320 nm	Blue / 485 nm
ZnS:Cu^+,Al^{3+}	<420 nm	Blue/ 520 nm
ZnS:Mn^{2+}	< 400 nm	Orange-yellow / 590 nm
ZnSe:Cu^+,Cl	<440 nm	Red / 650 nm
CdSe:Yb^{3+2}	< 600 nm	NIR / 985 nm

*Spectra data are adapted from Ref. 1 unless otherwise indicated.

Table S2 Selected examples of ET in ion pairs of RE or non-RE ions for enhanced Stocks emission

Sensitizer	Transition/position*	Activator: resonance energy level	Transition/position	Ref.
Ce^{3+}	$4f(^2F_J)\rightarrow 5d(A_{1g})$ / 320 nm (in most oxides) 450 nm (in YAG) 250 nm, 350 nm (in CaF_2)	Tb^{3+}: ^5D_j (j=0, 1, 2, 3, 4..)	$^5D_4\rightarrow ^7F_{5,4,3}$ / 545 nm	3
		Nd^{3+}: ^2H_j (j=9/2, 11/2), ^4D_j (j=1/2, 3/2, 5/2) or higher	$^4F_{3/2}\rightarrow ^4I_{11/2}$ / 888 nm $^4F_{3/2}\rightarrow ^4I_{9/2}$ / 1062 nm	4
		Er^{3+}: $^3P_{3/2}$, ^2G_j (j=7/2, 9/2)	$^4I_{13/2}\rightarrow ^4I_{15/2}$ / 1550 nm	5
		Mn^{2+}: $^4T_2$, $^4A_1$	$^4T_1\rightarrow ^6A_1$ / 500 - 570 nm	1,6
Eu^{2+}	Eu^{2+} in $Sr_3MgSi_2O_8$ 4f-5d transition / 440 nm	Mn^{2+}: $^4T_2$, $^4A_1$	$^4T_1\rightarrow ^6A_1$ / 680 nm	7
Yb^{3+}	$^2F_{7/2}\rightarrow ^2F_{5/2}$ / 980 nm	Er^{3+}: $^4I_{11/2}$	$^4I_{13/2}\rightarrow ^4I_{15/2}$ / 1550 nm	8
		Tm^{3+}: $^3H_5$	$^3H_4\rightarrow 4^3F_4$ / 1400 nm $^3F_4\rightarrow ^3H_6$ / 1800 nm	8
		Pr^{3+}: $^1G_4$	$^1G_4\rightarrow ^3H_5$ / 1300 nm	9
		Bi-center	Center: 1250 nm	10
		Ni^{2+}: $^3T_2(^3F)$	$^3T_2\rightarrow ^3A_2$ / 1300 nm	11
Cu^{2+}	$^2B_{1g}\rightarrow ^2B_{2g}$ / 600 – 800 nm	Yb^{3+}:$^2F_{5/2}$	$^2F_{5/2}\rightarrow ^2F_{7/2}$ / 1050 nm	12
Nd^{3+}	$^4I_{9/2}\rightarrow ^2H_{9/2}$, $^4F_{7/2}$ / 800 nm	Yb^{3+}:$^2F_{5/2}$	$^2F_{5/2}\rightarrow ^2F_{7/2}$ / 1020 nm	9
Nd^{3+}	$^4I_{9/2}\rightarrow ^2H_{9/2}$, $^4F_{7/2}$ / 800 nm	Er^{3+}: $^4I_{9/2}$	$^4I_{11/2}\rightarrow ^4I_{13/2}$ / 2700 nm	13
Tm^{3+}	$^3F_4$ / 1750 nm	Dy^{3+}: $^6H_{11/2}$	$^6H_{11/2}\rightarrow ^6H_{13/2}$/4300 nm $^6H_{13/2}\rightarrow ^6H_{15/2}$ 2900 nm	14

*f-f transition energies are almost independent of the types of host.

Table S3 Selected examples of sensitizer ions for the NIR emission of Yb^{3+} for QC in NIR range. (remove to SI)

ion	host	Excitation / emission wavelength (transition)	Mechanism Coop. / CR [a]	Ref.
Ce^{3+}	YAG	470 nm / 550 nm (4f-5d transition)	Coop.[b]	15
	Y_2SiO_5	360 nm / 431 nm	Coop.[b]	16
Pr^{3+}	oxide	442 nm, 489 nm ($^3H_4 \rightarrow ^3P_{2,1,0}$) / 607 nm ($^3P_0 \rightarrow ^3H_6$)	Both[c]	17-19
Nd^{3+}	YF_3	354 nm ($^4D_{1/2}$), 520 ($^4G_{11/2}$) / 880 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$) 1330 nm ($^4F_{3/2} \rightarrow ^4I_{13/2}$)	CR	20
Eu^{3+}	Oxyfluoride GC, ZrO_2	394 nm ($^5D_4$) / 590 nm, 615 nm ($^5L_6$/$^5D_0 \rightarrow F_{2,1,0}$)	Coop.	21
Tb^{3+}	$LaPO_4$	489 nm ($^7F_6 \rightarrow ^5D_4$) /540, 570, 620 nm ($^5D_4 \rightarrow ^7F_j$)	Coop.	22
Ho^{3+}	Tellurite GC	360 nm ($^5G_5$), 449 nm ($^5G_6$) / 550 nm, 660 nm ($^5S_2 \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$)	CR	23
Er^{3+}	La_2O_2S	523 nm ($^2H_{11/2}$) / 540 nm, 650 nm ($^4S_{3/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$), 1550 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$)	CR	24
Tm^{3+}		467-475 nm ($^1G_4$) / 650 nm ($^1G_4 \rightarrow ^3F_4$), 780 nm ($^1G_4 \rightarrow ^3H_5$)	Both[c]	18
Eu^{2+}	Borate glass	320nm / 440 nm (4f7-4f65d transition)	Coop.[b]	25
Cr^{3+}	YAG	450 nm ($^4T_1$), 590 nm ($^4T_2$) / $^2E \rightarrow ^4A_2$ 688 nm	Coop.[d]	26
Mn^{2+}	Zn_2GeO_4	370 nm ($^4A_1$(G), $^4T_2$(G))/ 535 nm ($^4T_1 \rightarrow ^6A_1$)	Coop.[d]	27
MoO_4^{2+}	$CaMO_4$	Charge transfer transition at 350 nm	Coop.	28
Bi^{3+}	Gd_2O_3	350 nm / 500 nm ($^3P_1 \rightarrow ^1S_0$)	Coop.	29
	YVO_4	350 nm/ 450 - 550 nm ($^3P_1 \rightarrow ^1S_0$)	Coop.	30

a. Coop.: cooperative energy transfer; CR: cross relaxation energy transfer.

b. The assignment of a cooperative has been questioned by other authors.

c. Both cooperative and CR have been proposed to explain the ET to Yb^{3+}.

d. High possibility of a one-to-one ET, not QC.

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