Electronic Supplementary Material (ESI) for Nanoscale.

# Supporting Information

## Lanthanide Doped Nanocrystals as Remote Sensor for Magnetic Field

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## 1. Experimental section

***Cheicals and Materials:*** chemical: $Y(Ac)_3 \cdot 4H_2O$ (99.99%), $Ho(Ac)_3 \cdot 4H_2O$ (99.99%) were purchased from Ansheng inorganic materials center Ganzhou in China. NaOH, $NH_4F$, 1-octadecene (ODE) (90%), and oleic acid (OA) (90%) were purchased from Sigma-Aldrich. Cyclohexane was purchased from Wako Pure Chemical Industries, Ltd. All of the chemicals were used as starting materials without further purification.

***Synthesis of $Eu^{3+}$ doped $NaYF_4$ nanoparticles （PNs）:*** the $NaYF_4$: 5% Eu nanoparticles were prepared according to the co-precipitate method reported by Xiaogang Liu with some modification.[1] In a typical procedure, $Y(Ac)_3 \cdot 4H_2O$ (3.80 mL) and $Eu(Ac)_3 \cdot 4H_2O$ (0.20 mL) were mixed with oleic acid (6 mL) and 1-octadecene (14 mL) in a three-neck round-bottom flask (50 mL). The resulting mixture was heated to 155 °C for 30 min to form a clear solution and then cooled down to room temperature. Thereafter, methanol solution (10 mL) containing $NH_4F$ (1.8 mmol) and NaOH (2.0 mmol) was added, and the solution was stirred at 50 °C for 30 min. After methanol was evaporated, the solution was heated to 290 °C under Ar flow with vigorous stirring for 90 min and then cooled down to room temperature. The obtained NPs were precipitated by ethanol, collected by centrifugation, washed with ethanol for several times, and finally redispersed in cyclohexane.

***Synthesis of ligand-free $NaYF_4$: 5% $Eu^{3+}$ NPs:*** the ligand-free $NaYF_4$ :5% $Eu^{3+}$ NPs were prepared according to the co-precipitation method reported by John A. Capobianco with some modification.[2] In a typical procedure, Oleate-capped $NaYF_4$:

5% $Eu^{3+}$ NPs (synthesis in section **1.1**) (100 mg) were dispersed in a aqueous solution (10 mL). The reaction was performed with stirring for 2 h while maintaining the pH at 3 by adding a solution of HCl (0.1 M). During this reaction the carboxylate groups of the oleate ligand were protonated (to yield oleic acid). After the reaction was completed the aqueous solution was mixed with diethyl ether to remove the oleic acid by extraction with diethyl ether three times and the combined ether layers were re-extracted with water. In addition, the water layers were combined and re-extracted with diethyl ether. The NPs in the water dispersible fraction were recuperated by centrifugation after precipitation with acetone. The product was redispersed in acetone and the particles were recuperated by centrifugation. Finally the particles were dispersed in water.

***X-Ray Diffraction (XRD):*** XRD pattern of the dry powder was obtained on a RIGAKU D/MAX 2550/PC diffractometer (Japan) with a slit of 0.02° at a scanning speed of 5° $min^{-1}$ using Cu Kα radiation ($\lambda = 1.5406$ Å).

***High-resolution Transmission Electron Microscopy (HRTEM):*** HRTEM analysis was performed on a FEG-TEM (Tecnai G2 F30 S-Twin, Philips-FEI, Netherlands) operated at 300 kV. Sample for HRTEM analysis were prepared by drying a drop of diluted solution of NPs in water on copper grids coated by amorphous carbon.

## 2. Fig. S1

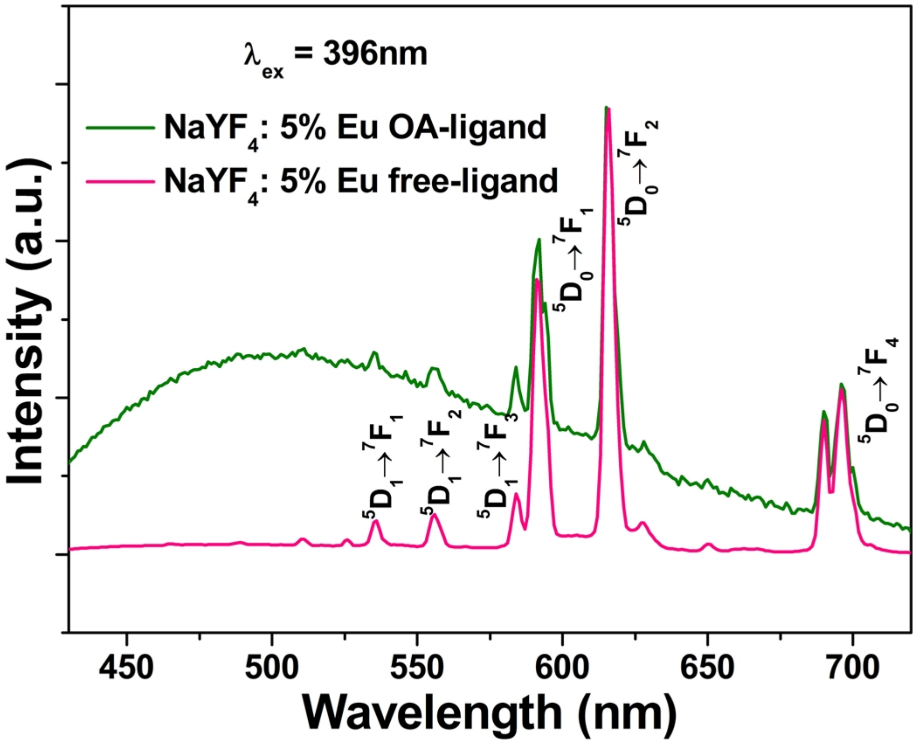

**Fig. S1** Photoluminescence spectra of $NaYF_4$: 5% Eu NPs with and without OA ligand.

## 3. Fig. S2

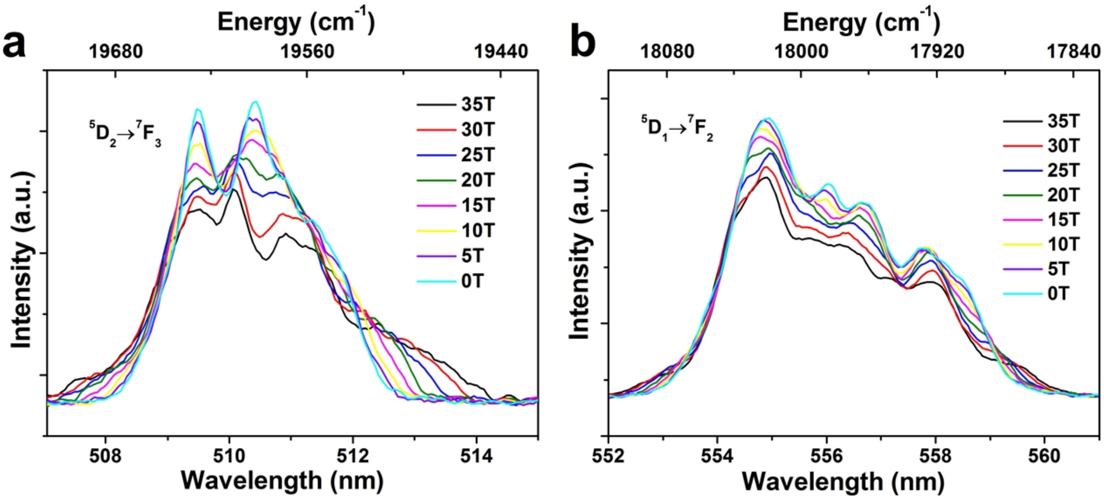

**Fig. S2** (a-b) Photoluminescence spectra from $NaYF_4$: 5% Eu NPs under the excitation of 396 nm laser with the transition of $^5D_2 \rightarrow {}^7F_3$ (a) and $^5D_1 \rightarrow {}^7F_2$ (b) of $Eu^{3+}$ with different MF intensity at 80 K.

## 4. Figure S3

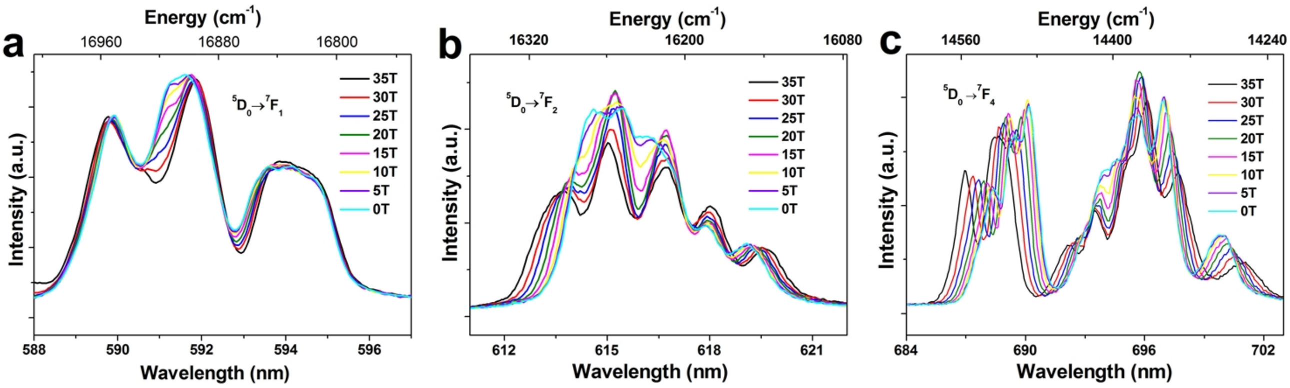

**Fig. S3** (a-c) Photoluminescence spectra from $NaYF_4$: 5% Eu NPs under the excitation of 396 nm laser with the transition of $^5D_0 \rightarrow {}^7F_1$ (a), $^5D_0 \rightarrow {}^7F_2$ (b) and $^5D_0 \rightarrow {}^7F_4$ (c) of $Eu^{3+}$ with different MF intensity at 80 K.

## 5. The effect of MF on the energy levels of Eu$^{3+}$.[3]

Orbital angular momentum of the electron is $P_L$. Orbital magnetic moment is $\mu_L$. Spin angular momentum is $P_S$. Spin magnetic moment is $\mu_S$.

$$P_L = \sqrt{L(L+1)h} \qquad (1)$$

$$\mu_L = \frac{e}{2mc} P_L \qquad (2)$$

$$P_S = \sqrt{S(S+1)h} \qquad (3)$$

$$\mu_s = \frac{e}{mc} P_S \qquad (4)$$

$e$, $m$ are the electric charge and mass of an electron. $L$, $S$ are orbital quantum number and spin quantum number. $P_J$ is the total angular momentum. $\mu$ is the total magnetic moment. $\mu_J$ is the effect total magnetic moment to total angular momentum.

$$\mu_J = g \frac{e}{2m} P_J \qquad (5)$$

$g$ is Lande factor.

After application of MF ($B$), an external torque ($L$) would be appeared, resulting in an external energy ($\Delta E$) to each energy level.

$$L = \mu_J \times B \qquad (6)$$

$$\Delta E = -\mu_J B \cos\beta \qquad (7)$$

$$\Delta E = g \frac{e}{2m} P_J B \cos\beta \qquad (8)$$

$$P_J \cos\beta = Mh \qquad (9)$$

$$\Delta E = Mg \frac{eh}{2m} B \qquad (10)$$

$M$ is magnetic quantum number, which has one of 2J+1 values, -J, -J+1, ... , J.

We define the energy before and after transition is $E_1$, $E_2$, and frequency of the luminescence is $\nu$. The external energy before and after transition is $\Delta E_1$, $\Delta E_2$ with

MF. The frequency of luminescence after application of MF is $\nu'$. The energy change in frequency is $\Delta\nu$. The energy change in wave-number is $\Delta\sigma$.

$$\nu = \frac{E_2 - E_1}{h} \tag{11}$$

$$\nu' = \frac{E_2 - E_1}{h} + \frac{\Delta E_2 - \Delta E_1}{h} \tag{12}$$

$$\Delta\nu = \nu' - \nu = \frac{\Delta E_2 - \Delta E_1}{h} = (M_2 g_2 - M_1 g_1)\frac{e}{2\pi m}B \tag{13}$$

$$\Delta\sigma = \nu' - \nu = \frac{\Delta E_2 - \Delta E_1}{h} = (M_2 g_2 - M_1 g_1)\frac{e}{2\pi mc}B \tag{14}$$

## 6. Table S1

**Table S1.** The energy of the $Eu^{3+}$ energy levels before and after the application of MF.

| Energy level | Energy (H = 0) ($cm^{-1}$) | Energy (H = 35T) ($cm^{-1}$) |
|---|---|---|
| $^7F_0$ | 0 | 0 |
| $^7F_1$ | 314 | 307 |
| | 353 | 364 |
| | 430 | 431 |
| $^7F_2$ | 994 | 968 |
| | 1017 | 1005 |
| | 1047 | 1048 |
| | 1083 | 1082 |
| | 1111 | 1122 |
| $^7F_3$ | 1850 | 1820 |
| | 1858 | 1845 |
| | 1893 | 1878 |
| | 1929 | 1911 |
| | 994 | 1939 |
| | 1017 | 1964 |
| | | 1989 |
| $^7F_4$ | 2738 | 2707 |
| | 2761 | 2744 |
| | 2777 | 2817 |
| | 2835 | 2845 |
| | 2856 | 2879 |
| | 2889 | 2899 |
| | 2917 | 2932 |
| | 2976 | 2998 |
| | | 3112 |
| $^5D_0$ | 17265 | 17265 |
| $^5D_1$ | 19019 | 19001 |
| | | 19024 |
| | | 19050 |

**7. Fig. S4**

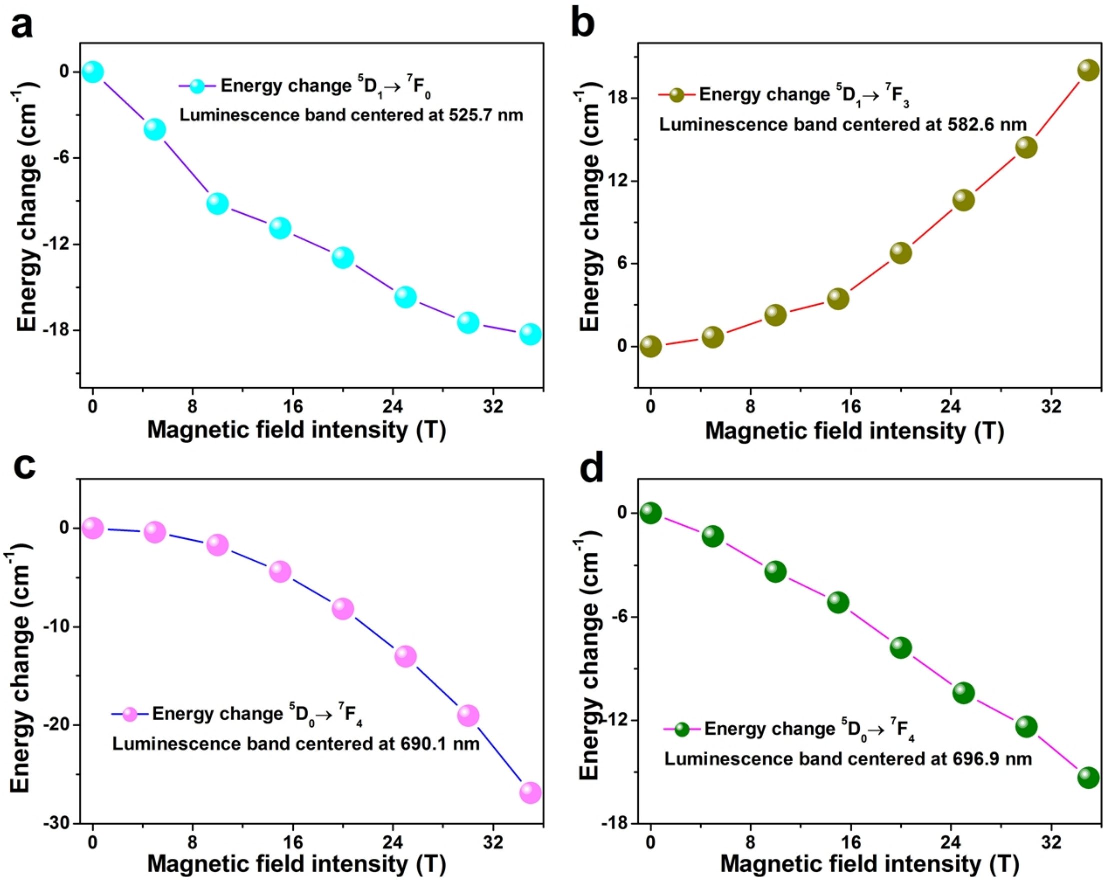

**Fig. S4** (a-d) Energy change of the luminescence bands centered around 525.7 nm (a), 582.6 nm (b), 690.1 nm (c) and 696.9 nm (d) with different MF intensity at 80 K.

## 8. Fig. S5

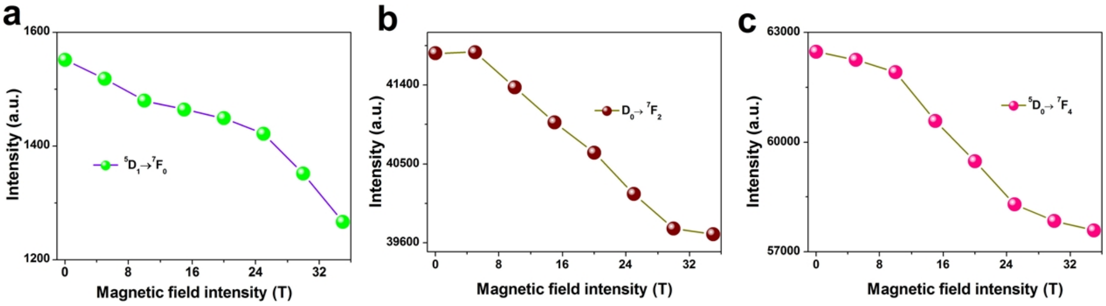

**Fig. S5** (a-c) Ddependence of integrated luminescence intensity on MF intensity for the transitions of $^5D_1 \rightarrow ^7F_0$ (a), $^5D_0 \rightarrow ^7F_2$ (b) and $^5D_0 \rightarrow ^7F_4$ (c) of $Eu^{3+}$ at 80 K.

## 9. Fig. S6

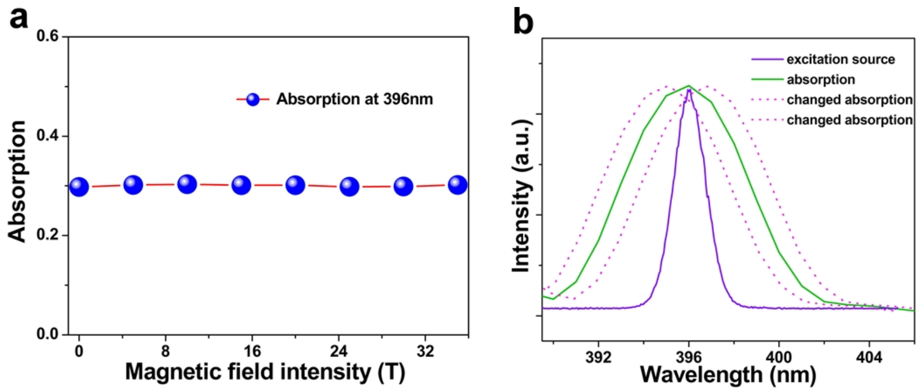

**Fig. S6 a)** Dependence of absorption at 396 nm on MF intensity. b) The absorption around 396 nm at 0 T, together with the line shape of the excitation laser beam. The absorption spectra with ±1 nm blue/red shift are provided as reference, to examine the possible change in the absorption in MF.

It is possible that absorption is affected by MF because Zeeman effect induces energy level splitting and blue/red shift. Since it is not possible to measure the absorption of NPs directly with the fiber-optical system, we instead recorded intensity of transmitted light through a glass-ceramic plate containing $NaYF_4$: 5% Eu NPs. **Fig. S6a** shows the absorption at 396 nm remains almost unchanged with increasing the applied MF. From **Fig. S6b**, assuming a ±1 nm blue/red shift of absorption around 396 nm, there is less than 1% change of absorption as calculated from overlapped areas of the absorption and excitation laser beam. The low resolution of absorption measurement setup might be unable to detect the very small change in absorption spectrum. In comparison, the reduction of emission intensity by MF is much higher than 1%. For instance, the reduction in intensity for $^5D_1 \rightarrow {}^7F_3$ is 34%, indicating the changing in absorption is not the main reason for the suppressed emission.

## 10. Fig. S7

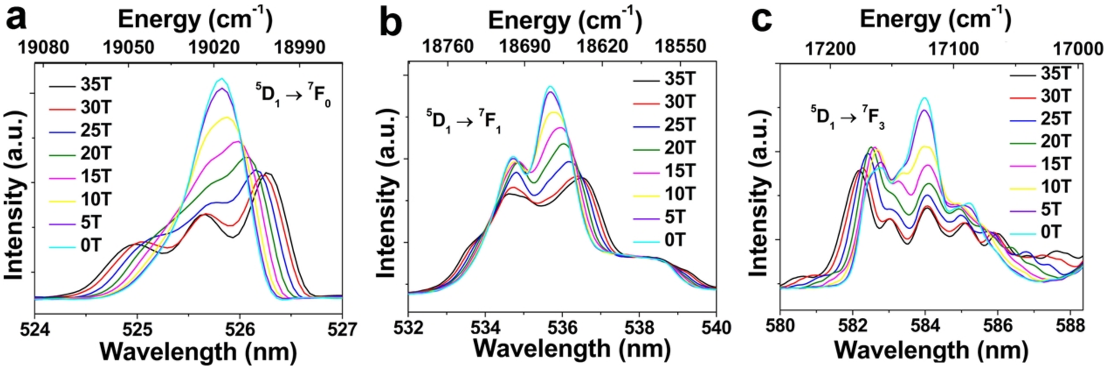

**Fig. S7** (a-c) Photoluminescence spectra from NaYF$_4$: 5% Eu NPs under the excitation by the 396 nm laser for the transition of $^5D_1 \rightarrow {}^7F_0$ (a), $^5D_1 \rightarrow {}^7F_1$ (b) and $^5D_1 \rightarrow {}^7F_3$ (c) of Eu$^{3+}$ with different MF intensity at 140 K.

## 11. Fig. S8

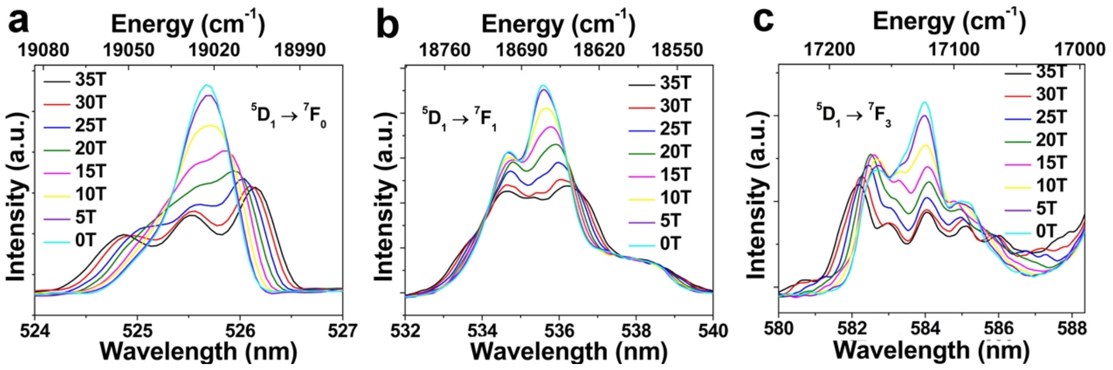

**Fig. S8** (a-c) Photoluminescence spectra from $NaYF_4$: 5% Eu NPs under the excitation of 396 nm laser with the transition of $^5D_1 \rightarrow {}^7F_0$ (a), $^5D_1 \rightarrow {}^7F_1$ (b) and $^5D_1 \rightarrow {}^7F_3$ (c) of $Eu^{3+}$ with different MF intensity at 250 K.

# References

[1] F. Wang, R. Deng, J. Wang, Q. Wang, Y. Han, H. Zhu, X. Chen, X. Liu, *Nat. Mater.,* 2011, **10**, 968.

[2] F. Liu, E. Ma, D. Chen, Y. Yu, Y. Wang, *J. Phys. Chem. B,* 2006, 110*,* 20843.

[3] G. W. F. Drake, in *Springer Handbook of Atomic, Molecular, and Optical Physics*, Vol. **2** (Eds: W. Martin, W. Wiese), Springer New York, New York, USA, 2006, pp. 175-198.